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A LABORATORY GUIDE
TO
CHEMICAL ANALYSIS.

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BY
DAVID O'BRINE, E.M., M.D., D.Sc.,

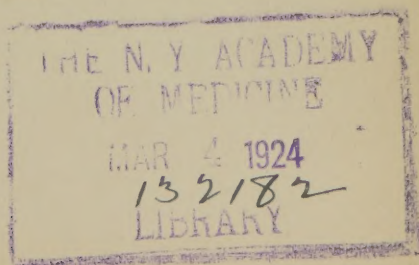
PROFESSOR OF CHEMISTRY AND GEOLOGY IN
COLORADO STATE AGRICULTURAL COLLEGE,
CHEMIST OF THE EXPERIMENT STATION.

"Longum iter est per praecepta, breve et efficax per exempla."—Seneca Ep. VI.

FOURTH EDITION,
ENTIRELY REWRITTEN AND REVISED.

NEW YORK:
JOHN WILEY & SONS,
53 EAST TENTH STREET.

1892.



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DAVID O'BRINE,

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TO
HIS ESTEEMED FRIEND AND TEACHER,
S. A. NORTON, PH. D., LL. D.,
PROFESSOR OF CHEMISTRY IN
OHIO STATE UNIVERSITY, COLUMBUS, OHIO,

THIS WORK
IS RESPECTFULLY DEDICATED BY
THE AUTHOR.

PREFACE TO THE SECOND EDITION.

This edition has been entirely rewritten, and is practically a new book. The chapter on reagents has been extended, so that it occupies nearly four times the original space. The uses, impurities, and tests for each reagent have been added. The tests in the dry way have been doubled, and are now presented in a more systematic form. To Prof. Eggleston, E. M., Ph. D., LL. D., of the School of Mines, Columbia College, I am indebted for the scheme of blowpipe analysis on pages 68 and 69. The tests in the wet way have been similarly enlarged, and a scheme for the separation by electrolysis has been added, by Prof. E. B. Knerr, A. M., D. Sc., of Parson's College, Iowa. The space allotted to the acids has been increased, thus enabling me to deal more fully with the subject. Chapter V. is entirely new. The facts, laws, etc., employed in chemistry have been compiled and presented in a convenient form. The comparison of the bases and acids, it is thought, will be found useful to the student. The chapter on water has been carefully read, both in manuscript and in proof sheets, by Prof. C. C. Howard,

PREFACE TO THE SECOND EDITION.

M. S., of Starling Medical College, Columbus, Ohio. His wide experience in water analysis has contributed largely to its value. The chapter on poisons has been very much enlarged, and to it the recovery of the more expensive reagents has been added. The chapter on stoichiometry has been extended by adding the heating power of coal. This chapter has been read, in manuscript and in proof sheets, by Prof. Floyd Davis, M. S., Ph. D., of Drake University, Iowa, and I have profited by his valuable suggestions.

My thanks are due to all who have aided me in any way, by criticism or by words of advice; but especially am I under obligations to my friend and teacher, Prof. S. A. Norton, Ph. D., LL. D., of the Ohio State University, Columbus, O. He has carefully and patiently read the entire work in manuscript and in proof, and to him I am indebted for much of its value and accuracy. Any corrections or queries from those using the book shall have my grateful attention.

FORT COLLINS, August, 1888.

PREFACE.

This little volume is intended for the use of students who possess some knowledge of Chemistry. The object is to present a practical guide in Chemistry adapted to the wants of the College or the Medical Laboratory. It would be impossible to acknowledge the sources of all analytical details or methods; they have been used, and in most cases modified by so many different persons that they are now regarded as common property. The labors of many well known chemists have been laid under contribution. Some of the methods are my own, *and every test presented has been verified.* There is a discussion of all that is important in the analysis of water, milk and cheese, blood, urine, and poisons. Especial attention is invited to the following subjects: Separation of Bases, and tests; Comparison of Phosphorus, Arsenic, and Antimony; The Organic Acids; Classification of the Alkaloids; The Ptomaines; and Stoichiometry.

My thanks are due to the students and faculty of the Columbus Medical College, and especially to Drs.

PREFACE.

HAMILTON, KINSMAN, LEE, and POOLEY, for their kindness and assistance. I am under special obligations to Prof. NORTON, LL. D., of the Ohio State University, for much kind advice and assistance with the proof and many of the tests.

The work is presented to the Laboratory student, hoping it may lessen his labor.

OHIO STATE UNIVERSITY, Columbus, May, 1883.

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LABORATORY GUIDE.

PREPARATION OF REAGENTS.

ACIDS.

Acids are used as general solvents, both in the concentrated and dilute states. The dilute acid generally contains from three to five molecules of H_2O to one of the acid.

To neutralize alkaline solutions. Care should always be taken not to add a great excess of acid.

The higher oxygen acids, as HNO_3 , HClO_3 , are used as oxidizing agents, as are also their salts when mixed with free HCl or H_2SO_4 , as $\text{K}_2\text{Mn}_2\text{O}_8$, KClO_3 .

The weak acids, as acetic acid, or their salts, as sodium acetate, are sometimes used in analyses, as in the separation of ZnS from the bases of the iron group.

Some organic acids, as tartaric and citric, are used to prevent or hinder the precipitation of the oxides of the iron group.

In a mixture of bases and acids it is generally considered that the strong bases are united with the strong acids; if an acid be free, it is presumably a weak acid.

1. Acetic acid ($\text{H}, \text{C}_2\text{H}_3\text{O}_2$), sp. gr. 1.04, contains 30 per cent. acid.

PREPARATION—Made by allowing 8 per cent. alcohol to trickle slowly over hard wood shavings in a free circulation of air; also as a bye product from the destructive distillation of wood.

TESTS—On heating an acetate in a tube, the odor of *acetone* will be perceived. Heat an acetate with alcohol and sulphuric acid, and acetic ether will be given off.

IMPURITIES—It may be contaminated by H_2SO_4 , HCl , or HNO_3 , and should yield none of the tests which are used for their detection.* This will apply to the impurities in *all* the reagents.

USES—To acidulate fluids when it is wished to avoid the employment of mineral acids. In separations, as follows: it dissolves calcium phosphate, but does not dissolve calcium oxalate, distinguishing the former from the latter; it also dissolves manganese sulphide, but does not dissolve zinc sulphide.

2. Arsenic (As_2O_5), **3. Arsenious** (As_2O_3) **anhydrides.**
 $\text{As}_2\text{O}_5 + 3\text{H}_2\text{O} = 2(\text{H}_3\text{AsO}_4)$ and $\text{As}_2\text{O}_3 + 3\text{H}_2\text{O} = 2(\text{H}_3\text{AsO}_3)$
acids.

PREPARATION—The As_2O_3 is prepared by roasting arsenical pyrites in muffle furnaces through which the air is allowed to pass, and is condensed as a fine white powder. The arsenic acid is prepared by oxidizing arsenious anhydride (As_2O_3) with nitric acid— $\text{As}_2\text{O}_3 + 2\text{HNO}_3 + 2\text{H}_2\text{O} = \text{N}_2\text{O}_3 + 2(\text{H}_3\text{AsO}_4)$.

TESTS—When heated on charcoal, it gives a garlic odor. In solution As_2O_3 with AgNO_3 yields yellow Ag_3AsO_3 .† As_2O_5

*In general terms it may be said that the probable impurities in any reagent may be inferred from the materials used in the manufacture of that reagent.

†In this book the sign — placed over a symbol indicates that a gas is produced or evolved; the same sign — placed under a symbol indicates that a solid is formed and precipitates.

with AgNO_3 yields red brown Ag_3AsO_4 . Marsh's and Davy's (NaHg) tests are very delicate.

IMPURITIES—When in powder (As_2O_3 or As_2O_5) it may contain powdered chalk or sulphate or arsenite of calcium. These substances can be detected by vaporizing the arsenic, when the impurities will be left behind. The vitreous is the purest.

USES—Arsenious acid is employed in the form of arsenite of soda to determine hypochlorous acid, free chlorine, and iodine. The arsenic acid is used as an oxidizing agent.

4. Boric anhydride (B_2O_3) and borax, baborate of soda, ($\text{Na}_2\text{B}_4\text{O}_7, 10\text{H}_2\text{O}$). Borax is found native as *tinca*. Boric acid is found native as *sassolite*.

PREPARATION—Boric acid is made by dissolving borax in hot water, and adding strong HCl , when white, pearly looking scales of H_3BO_3 separate out on cooling.

TESTS—Free boric acid imparts a green tinge to the colorless flame of a Bunsen lamp. The same color may be obtained from a borate by previously moistening it with strong sulphuric acid or with glycerin.

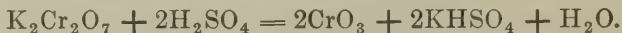
IMPURITIES—Borax may contain H_2SO_4 , HCl , Pb , Cu , Fe , Ca , or NaCl .

USES—The principal use of borax is for a flux; it dissolves metallic oxides, with the formation of colored beads. Fused borax is used for the determination of CO_2 and HNO_3 by loss. For blowpipe work the crystallized borax is exposed to a gentle heat in a crucible until it ceases to swell. Cool, and pulverize, when it is ready for use.

5. Chromic acid (H_2CrO_4) has never been isolated. Potassium chromate (K_2CrO_4) and bichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) are quite important.

PREPARATION—Pulverized chrome iron ore is mixed with potassium carbonate and potassium nitrate, and is then heated in a current of air in a furnace. The Cr_2O_3 is oxidized to

2CrO_3 , and unites with the potassium to form potassium chromate. When potassium chromate is treated with nitric acid, potassium bichromate is formed— $2\text{K}_2\text{CrO}_4 + 2\text{HNO}_3 = 2\text{KNO}_3 + \text{H}_2\text{O} + \text{K}_2\text{Cr}_2\text{O}_7$. When a cold saturated solution of potassium bichromate is treated with sulphuric acid, the anhydride CrO_3 separates out, as follows:



TESTS—A solution of potassium bichromate treated with acetate of lead forms *yellow* PbCrO_4 . A solution of CrO_3 treated with hydrogen peroxide and ether gives a fine *blue* color.

IMPURITIES—The $\text{K}_2\text{Cr}_2\text{O}_7$ may contain K_2CrO_4 or HNO_3 , and the CrO_3 may contain H_2SO_4 or KHSO_4 .

USES— CrO_3 is a powerful oxidizing agent: $2\text{CrO}_3 = \text{Cr}_2\text{O}_3 + \overline{\text{O}_3}$. Heated with H_2SO_4 , $\overline{\text{O}}$ is set free; heated with HCl , $\overline{\text{Cl}}$ is liberated, or chlorochromic acid. A solution of K_2CrO_4 is used as an indicator in volumetric analysis. A solution of $\text{K}_2\text{Cr}_2\text{O}_7$ in free H_2SO_4 is used in volumetric analysis for an oxidizing agent, as in the determination of iron.

6. Citric acid (H_3 , $\text{C}_6\text{H}_5\text{O}_7$, H_2O), a 10 per cent. solution.

PREPARATION—It is made from lemon juice, which contains the acid in the free state (about 5 per cent), by boiling to coagulate the albuminous matters, treating with CaCO_3 , and decomposing the $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2$ with H_2SO_4 , filtering and evaporating.

TESTS—It melts when heated, and at 175°C . gives off pungent characteristic vapors containing acetone, while aconitic acid is formed in the residue. AgNO_3 gives a white precipitate, $\underline{\text{Ag}_3(\text{C}_6\text{H}_5\text{O}_7)}$, which does not blacken on boiling (distinction from tartrate).

IMPURITIES—It may contain tartaric, oxalic, or sulphuric acids, and the metals lead, copper, and iron.

USES—It prevents or hinders the precipitation of the metals by the alkaline hydroxides.

7. Potassium ferricyanide ($K_3FeC_6N_6$), one part of the salt to twelve parts of water. It should not be dissolved until wanted.

PREPARATION—It is made by oxidizing $K_4FeC_6N_6$ by Cl until the solution will no longer give a precipitate with a ferric salt. It has a red color.

TESTS—It gives Turnbull's blue, $Fe_3(FeC_6N_6)_2$, when treated with *ferrous* salt; with ferric salt it gives no precipitate, but the solution becomes brown.

IMPURITIES—It may contain Cl or $K_4FeC_6N_6$.

USES—For the detection of ferrous salts and as an indicator in volumetric analysis; also as an oxidizing agent in the presence of alkaline hydroxides.

8. Potassium ferrocyanide ($K_4FeC_6N_6 \cdot 3H_2O$), one part of the salt to twelve parts of water.

PREPARATION—By heating animal matter with iron filings and K_2CO_3 , which results in the formation of KCN. On lixiviating the fused mass with hot water, the KCN acts upon the iron oxide and iron sulphide simultaneously produced by the roasting, and then results in the formation of potassium ferrocyanide, which crystallizes out.

TESTS—It forms Prussian blue, $Fe_4(FeC_6N_6)_3$, when treated with ferric salts, and with copper it forms a dark brown precipitate of cupric ferrocyanide, $Cu_2FeC_6N_6$. It forms with most of the metals colored solutions or precipitates.

IMPURITIES—It may contain CO_2 , H_2SO_4 , HCl.

USES—To make ferricyanide as above described; also to make hydrocyanic acid, and as a general reagent.

9. Gallic acid ($C_7H_6O_5, H_2O$).

PREPARATION—Mix powdered nutgalls with water to form a thin paste, and expose the mixture to the air in a warm place for thirty days; filter, reject the filtrate, boil the residue with water, and filter through animal charcoal; set the liquid aside to crystallize and dry on bibulous paper.

TESTS—Add a few drops of potassium hydroxide to gallic acid, and an intense green color is produced. This color is changed to purple red by acids, and is prevented by an *excess* of alkaline hydroxide or carbonate. The above reaction (*green*) does not occur with gallotannic or pyrogallic acid. An aqueous solution of the acid should not precipitate alkaloids, gelatin, albumin, gelatinized starch, nor a solution of tartrate of antimony and potassium previously mixed with chloride of ammonium (distinction from tannic acid).

IMPURITIES—Tannic acid.

USES—To make pyrogallic acid. When gallic acid, in the absence of water, is heated to 215°C ., it is sublimed as pyrogallic acid and carbonic anhydride; at higher temperatures other products are formed: $\text{C}_7\text{H}_6\text{O}_5 = \text{C}_6\text{H}_6\text{O}_3 + \text{CO}_2$.

10. Hydriodic acid (HI), an aqueous solution.

PREPARATION—Pass H_2S through water in which iodine is suspended, $\text{H}_2\text{S} + \text{I}_2 = 2\text{HI} + \text{S}$. Filter off the S, and boil to expel the excess of H_2S . It is decomposed by exposure to the air.

TESTS— AgNO_3 precipitates yellowish white AgI, blackening in the light. HgCl_2 precipitates yellowish red HgI₂. PdCl_2 precipitates black PdI₂.

IMPURITIES—Free iodine, which may be known by the solution turning a brownish yellow color.

USES—The tendency of H of HI to combine with O renders that acid a powerful *reducing* agent.

11. Hydrobromic acid (HBr), an aqueous solution.

PREPARATION—By allowing Br and P to act on one another in the presence of water: $3\text{H}_2\text{O} + 3\text{Br} + \text{P} = \text{H}_3\text{PO}_3 + 3\text{HBr}$. It is decomposed by exposure to the air.

TESTS—When a bromide is treated with $\text{H}_2\text{SO}_4 + \text{MnO}_2$, it gives off Br. In solution HgNO_3 precipitates Hg₂Br₂, yellowish

white, soluble in excess of alkaline bromides. Bisulphide of carbon, chloroform, or ether gives, with free Br, a reddish yellow solution; free Br colors starch solution orange yellow.

IMPURITIES—Free bromine.

USES—Most metals and their oxides are dissolved by it.

12. Hydrochloric acid (HCl), sp. gr., 1.12; contains 24 per cent. acid. The dilute acid is made by adding one part of acid to three parts of water.

PREPARATION—Made by heating *fused* common salt with sulphuric acid: $2\text{NaCl} + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 2\text{HCl}$.

TESTS— AgNO_3 gives a white precipitate of AgCl , insoluble in HNO_3 and soluble in NH_4HO . When a chloride is heated with $\text{MnO}_2 + \text{H}_2\text{SO}_4$, $\overline{\text{Cl}}$ is given off. Test by physical properties.

IMPURITIES—It may contain Fe, As, Cl, SO_2 , and H_2SO_4 .

USES—It is a group reagent for Ag, Pb, and Hg'. It is a good test for free ammonia, forming white clouds of $\overline{\text{NH}_4\text{Cl}}$. It dissolves most metals and their oxides, carbonates, and sulphides. When HCl dissolves the metals, $\overline{\text{H}}$ is liberated; when it dissolves the sulphides, $\overline{\text{H}_2\text{S}}$ is evolved. The peroxides, when treated with dilute HCl, fall into two groups, one evolving Cl as PbO_2 , MnO_2 ; the other producing H_2O_2 , as BaO_2 .

Aqua regia is $3\text{HCl} + \text{HNO}_3 = \left\{ \begin{array}{c} \text{NOCl}_2 + \text{Cl} \\ \text{or} \\ \text{NOCl} + \text{Cl}_2 \end{array} \right\} + 2\text{H}_2\text{O}$.

The solvent action is due to the free chlorine.

13. Hydrocyanic acid (HCN or HCy).

PREPARATION—Two parts of the ferrocyanide of potassium in powder are distilled with one and one-half parts of sulphuric acid diluted with two parts of water, the vapor of HCN being *carefully* condensed. Prepared in this way it contains a very small quantity of H_2SO_4 .

TESTS—When HCN is mixed with an equal quantity of $(\text{NH}_4)_2\text{S}$, and evaporated to dryness by a gentle heat, ammonium sulphocyanate is formed, which gives with the ferric salt a blood red solution.

IMPURITIES— H_2SO_4 and $\text{K}_4\text{FeC}_6\text{N}_6$.

USES—To separate Co from Ni. In electroplating and gilding.

14. Hydrofluoric acid (HF).

PREPARATION—By treating fluor spar with strong sulphuric acid— $\text{CaF}_2 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + 2\text{HF}$. The commercial acid, of a sp. gr. of 1.15, has the formula $\text{HF}, 2\text{H}_2\text{O}$.

TESTS—When free, it etches glass.

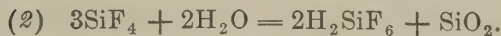
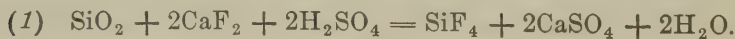
IMPURITIES—The commercial acid may contain H_2SO_4 .

USES—To decompose silicates and to etch glass.

NOTE—The following mixture will be found very convenient for marking beakers, as it deadens the surface, so that a lead pencil can be used to write on it. Mix equal parts of dry, recently precipitated BaSO_4 and NH_4F in a porcelain mortar, and add, while stirring, liquid hydrofluoric acid. Keep in a gutta percha bottle, shake before using, and expose about fifteen minutes. Use a steel pen to write on glass with this "diamond ink."

15. Hydrofluosilicic acid (H_2SiF_6).

PREPARATION—Heat a mixture of sand and fluor spar with sulphuric acid. The SiF_4 is passed first through a small vessel containing mercury and then through water:



TESTS—It forms difficultly soluble salts with potassium (K_2SiF_6) and barium (BaSiF_6), and is sometimes used to separate these elements from their soluble compounds.

IMPURITIES—It may contain H_2SO_4 .

USES—As tests for K and Ba. The addition of alcohol increases the insolubility of the precipitates.

16. Hydrosulphuric acid (H_2S), water saturated with the H_2S , made as required for use.

PREPARATION—Treat ferrous sulphide* with dilute sulphuric acid— $\text{FeS} + \text{H}_2\text{SO}_4 = \text{FeSO}_4 + \overline{\text{H}_2\text{S}}$: if the gas is passed through a saturated solution of water and glycerin, it will keep for six or eight months; the glycerin does not interfere with any reaction.

TESTS—The odor of rotten eggs. $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ gives a black PbS; AgNO_3 gives *black* Ag_2S .

IMPURITIES—When made from FeS it may contain As . In examination for poisons, prepare it from native sulphide of antimony and HCl .

USES—Besides its reducing action, it is largely employed as a group reagent.

17. Nitric acid (HNO_3), sp. gr. 1.2, contains 30 per cent. acid. A stronger acid is sometimes required, sp. gr. 1.52.

PREPARATION—By heating a nitrate with sulphuric acid:



TESTS—All the normal nitrates are soluble in water. Brucine gives a red color with HNO_3 ; ferrous sulphate with sulphuric acid gives a brown ring; pyrogallie acid when added to water acidulated with H_2SO_4 gives a brown zone of contact (very delicate).

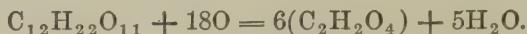
IMPURITIES—It may contain HCl , H_2SO_4 . It should be colorless and leave no residue when evaporated.

USES—It dissolves most of the metals to form nitrates (Sb and Sn form oxides). It is one of the best oxidizing agents.

18. Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$), one part of the acid to ten parts of water.

* FeS is made on a small scale by heating iron white hot in a blacksmith's forge, and running it through sulphur, and collecting the product in water; dry, and it is ready for use: $\text{Fe} + \text{S} = \text{FeS}$.

PREPARATION—By the action of nitric acid on sugar or of the alkalies on sawdust:



By this commercial method, the sawdust yields about one-half its weight of crystallized oxalic acid.

TESTS—When heated it breaks up into H_2O , CO , and CO_2 . All the soluble calcium salts produce in solutions of $\text{H}_2\text{C}_2\text{O}_4$ white, finely pulverulent $\text{CaC}_2\text{O}_4 + 3\text{H}_2\text{O}$, which is nearly insoluble in $\text{H}_2\text{C}_2\text{O}_4$; the addition of ammonia promotes the precipitation.

IMPURITIES—It may contain Ca , K , or HNO_3 .

USES—It is a good *reducing* agent; also used in volumetric estimations, particularly of the alkalies; also to standardize a solution of permanganate of potassium.

19. Permanganic acid ($\text{H}_2\text{Mn}_2\text{O}_8$) or potassium permanganate ($\text{K}_2\text{Mn}_2\text{O}_8$).

PREPARATION—Fuse MnO_2 with KNO_3 , which gives potassium manganate, K_2MnO_4 ; this is easily decomposed by water, forming a rose red solution of permanganate, $\text{K}_2\text{Mn}_2\text{O}_8$.

TESTS—A ferrous salt in the presence of *free* H_2SO_4 bleaches a solution of permanganate.

IMPURITIES—It may contain HNO_3 , HCl , H_2SO_4 , or NH_3 .

USES—It is one of the best oxidizing agents, and one of the most valuable reagents in volumetric analysis. As it is easily decomposed by organic substances, its solutions must be filtered through previously ignited asbestos or sand.

20. Picric acid ($\text{HO C}_6\text{H}_2(\text{NO}_2)_3$) a saturated alcoholic solution.

PREPARATION—When carbolic acid is boiled with fuming nitric acid, the solution, on cooling, deposits beautiful yellow crystals of carbazotic or picric acid.

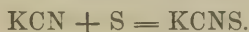
TESTS—Solutions of salts of K and of most of the *alkaloids* precipitate picric acid, or a solution of its soluble salts. The cinchona alkaloids give a *yellow* precipitate.

IMPURITIES—It may contain carbolic acid or nitric acid.

USES—An important reagent for the alkaloids. A test for potassium salts, rendered more sensitive by the addition of alcohol. One of the most delicate tests for albumin in urine, forming a white line at junction of the liquids. Potassium picrate explodes violently both by heating and by percussion.

21. (a) Potassium sulphocyanate (KCNS), one part of the salt in twenty parts of water.

PREPARATION—Fuse cyanide of potassium with sulphur:



(b) Ammonium sulphocyanate (NH_4CNS), one part of the salt in twenty parts of water.

PREPARATION—By digesting HCN with yellow ammonium sulphide: $(\text{NH}_4)_2\text{S} + 2\text{HCN} = 2(\text{NH}_4\text{CNS}) + \text{H}_2\text{S}$.

TESTS—Both are delicate tests for the ferric salts, giving with them a blood red solution.

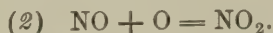
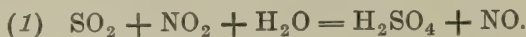
IMPURITIES—It should be remembered that the above reaction is masked by the presence of non-volatile organic acids. Almost every specimen of potassium sulphocyanate gives a red tint on the addition of pure H_2SO_4 or HCl ; this tint is prevented by adding a small piece of zinc. A solution of potassium sulphocyanate thus prepared can alone be safely employed as a test for small traces of ferric salt.

USES—They serve as indirect tests for S and HCN.

22. Sulphuric acid (H_2SO_4). The concentrated has a sp. gr. of 1.842; the Nordhausen ($\text{H}_2\text{S}_2\text{O}_7$), sp. gr. 1.9.

PREPARATION—By burning S or FeS_2 , and allowing the product of combustion, SO_2 , to mix with H_2O and NO_2 , obtained from the decomposition of NaNO_3 , which changes

SO₂ into H₂SO₄. The NO₂ becomes reduced to NO, but in the air becomes again NO₂. This continuous reaction may be represented as follows:



TESTS—BaCl₂ gives a *white* precipitate, BaSO₄, insoluble in dilute acids. Free sulphuric acid is detected by its property of charring sugar.

IMPURITIES—It may contain Pb, Cu, As, Fe, HNO₃, HCl, SO₂, and NO₂.

USES—It is used to decompose very many compounds, thereby evolving volatile products like HCl, HNO₃, and H₂S, or anhydrides like CO₂ and CrO₃. The difficultly soluble sulphates are those of Pb, Ba, Sr, and Ca; for these elements it is an especial reagent. The dilute acid is made by pouring the concentrated acid into four parts of water (not conversely).

23. Sulphurous anhydride (SO₂), solution in water.

PREPARATION—By heating H₂SO₄ with C or S:



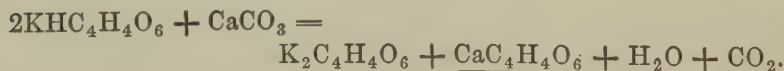
TESTS—When free, the odor is characteristic. When a few drops of a solution of its salt are treated with dilute HCl and Zn, H₂S is evolved.

IMPURITIES—H₂SO₄, as the SO₂ is easily oxidized to H₂SO₄.

USES—As a reducing agent, and in iodometric analysis.

24. Tartaric acid (H₂C₄H₄O₆). Dissolve the crystals in three parts of water when needed for use.

PREPARATION—Argols are boiled with powdered chalk, forming an *insoluble* calcium tartrate and a *soluble* potassium tartrate:



Calcium chloride is now added to the solution, when all the tartaric acid is precipitated as calcium tartrate:



The calcium tartrate is boiled with dilute H_2SO_4 , when an *insoluble* calcium sulphate and a solution containing free tartaric acid are formed:



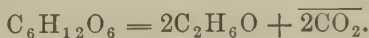
TESTS—When heated it gives off the odor of burnt sugar. A solution of $\text{KC}_2\text{H}_3\text{O}_2$ precipitates from concentrated solutions of tartaric acid the acid potassium tartrate, insoluble in alcohol (distinction and separation from citric, oxalic, and malic acids).

IMPURITIES—Pb, Cu, Fe, and H_2SO_4 .

USES—The same as citric acid.

25. Ethyl alcohol ($\text{C}_2\text{H}_6\text{O}$), sp. gr. .815.

PREPARATION—Made by the fermentation of grape sugar:



If 95 per cent. alcohol is treated with CaO a number of times, and then with metallic Na, a nearly pure *absolute* alcohol can be obtained.

TESTS—Add to the solution to be tested a few drops of a 10 per cent. solution of KHO , and warm to 50°C . A solution of I in KI is added until the solution becomes yellowish brown; to it add *cautiously* caustic alkali to decolorize it; if alcohol is present, a *yellow* precipitate is formed after a time (iodoform crystals).

IMPURITIES—It may contain fusel oil and water. The first can be recognized by its characteristic odor on evaporating a few drops on the hands. The absence of water may be known by the alcohol remaining clear when mixed with an equal bulk of pure benzol. Increased specific gravity will also indicate impurities.

USES—As a solvent for some substances, as LiCl. It is sometimes added to aqueous solutions to render precipitation more complete, as 2KCl, PtCl₄. It forms acetic ether with free acetic acid.

26. Ammonium carbonate (2(NH₄)₂O, 3CO₂), one part of the salt in four parts of water, and one part of ammonia.*

PREPARATION—Made by heating a mixture of ammonium chloride and calcium carbonate:



TESTS—It gives off the odor of ammonia, and effervesces with HCl, $\overline{\text{CO}_2}$ being given off. It should volatilize completely.

IMPURITIES—It may contain H₂SO₄ and HCl. It may also contain empyreumatic substances.

USES—It is advantageously used in the place of Na₂CO₃, because it is volatile. It is a group reagent for the alkaline earths. It separates arsenious sulphide from the antimonous sulphide, by dissolving the former but not the latter.

27. Ammonium chloride (NH₄Cl), one part of the salt to eight parts of water.

PREPARATION—When nitrogenous substances are subjected to destructive distillation, an impure ammonium carbonate is formed; this, when treated with HCl, forms NH₄Cl. This is afterwards sublimed.

TESTS—It should leave no fixed residue on evaporation on platinum. It gives a *brown* precipitate with Nessler's test for ammonia, and a white precipitate of AgCl with AgNO₃.

IMPURITIES—It commonly contains iron; If it contains iron, pass Cl through a saturated solution for a *short* time; add a slight excess of NH₄HO, warm, and filter. It may contain H₂SO₄ and Ba.

*When used as a solvent for arsenious sulphide, the ammonia is omitted.

USES—It forms very soluble double salts with certain elements, thereby preventing their precipitation, as Mn and Mg. It is used to precipitate from their solutions in potassium hydroxide various substances which are soluble in that alkali, but insoluble in ammonia, as alumina and chromic oxide. It is a special reagent to effect the precipitation of platinum as ammonium platinic chloride. It is used in the method of fluxing silicates for the separation of the alkali metals, and in the manufacture of ammonia.

28. Ammonium ferrous sulphate $((\text{NH}_4)_2\text{Fe}2(\text{SO}_4), 6\text{H}_2\text{O})$.

PREPARATION—Made by mixing solutions of the molecular weights of ferrous sulphate and ammonium sulphate; evaporating and crystallizing the salt.*

TESTS—In the presence of free H_2SO_4 it bleaches a solution of $\text{K}_2\text{Mn}_2\text{O}_8$. The presence of ammonia, iron, and sulphuric acid can be shown by their respective tests.

IMPURITIES—It ought to give no reaction for a ferric salt.

USES—A very important volumetric reagent. It is used to standardize $\text{K}_2\text{Mn}_2\text{O}_8$ and $\text{K}_2\text{Cr}_2\text{O}_7$.

29. Ammonium fluoride (NH_4F) .

PREPARATION—To hydrofluoric acid add ammonium to strong alkaline reaction (it is best to do this in a platinum dish); heat gently, filter, and evaporate to dryness. Keep in a gutta-percha bottle.

TESTS—A portion heated on platinum should leave no fixed residue; this test should be applied under good ventilation. It gives the tests for NH_3 and HF .

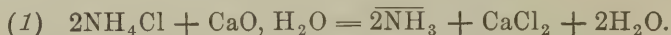
*The following general statement can be made: Double salts are prepared (1) by mixing together solutions of two salts in equivalent proportions, or (2) by fusion of the two salts.

IMPURITIES—If it leaves no residue, *especially* of SiO_2 , any other impurity can be neglected.

USES—This preparation may be very advantageously substituted for hydrofluoric acid in the analysis of silicates.

30. Ammonium hydroxide* (NH_4HO), sp. gr. 96; contains 10 per cent. NH_3 .

PREPARATION—Ammonium chloride is heated with slaked quicklime, and the gas passed into cold water:



TESTS—The odor, or by turmeric paper. For traces, Nessler's test gives a brown precipitate.

IMPURITIES—It should leave no residue on evaporation in a platinum dish. It may contain CO_2 , HCl , H_2SO_4 , Ca , and empyreumatic matter.

USES—To neutralize acids. To precipitate many metallic hydroxides; of these, some are soluble in an excess, as Zn , Cd , Ag , and Cu , while others are not soluble, as Fe . In *acid* solutions double salts may be formed that would hinder the precipitation, which might be formed in neutral solutions, as free HCl with NH_4HO forms NH_4Cl , which prevents the precipitation of magnesium. When NH_4HO neutralizes acid solutions, it enters into combination not only with the free acids, but also frequently displaces and combines with those previously in combination with other bases. These reactions give rise to salts which frequently have the remarkable property of forming with analogous salts of the heavy metals, double salts which are so easily soluble that it is commonly said that ammonium chloride hinders or prevents precipitation of the protoxides of the iron group.

*This body has never been obtained in a solid state, but it is convenient to reckon it analogous to potassium hydroxide.

31. Ammonium molybdate $((\text{NH}_4)_2\text{MoO}_4)$.

PREPARATION—Dissolve one gram of molybdic anhydride, MoO_3 , in four cubic centimeters of ammonia; pour into fifteen cubic centimeters of HNO_3 (sp. gr. 1.2).

TESTS—Phosphoric acid gives in presence of HNO_3 a *yellow* precipitate of ammonium phosphomolybdate of variable composition.

IMPURITIES—The MoO_3 may contain Pb or Fe.

USES—To precipitate phosphoric and arsenic acids, which are nearly insoluble in nitric acid. *Sodium phosphomolybdate* is soluble in water, and forms a delicate reagent for alkaloids (Sonnenschein's reagent).

32. Ammonium nitrate (NH_4NO_3) .

PREPARATION—Neutralize carbonate of ammonia with nitric acid; warm, and add ammonia to slight alkaline reaction; filter and crystallize. Fuse in a platinum dish.

IMPURITIES—It may contain any of the impurities of carbonate of ammonia or of ammonia. The salt should leave no residue when heated in a platinum dish.

TESTS AND USES—It serves as an oxidizing agent; to convert lead into the oxide of lead, or to effect the combustion of carbon in cases where it is desired to avoid the use of fixed salts. Also to make nitrous oxide: $\text{NH}_4\text{NO}_3 = \overline{\text{N}_2\text{O}} + 2\text{H}_2\text{O}$.

33. Ammonium oxalate $((\text{NH}_4)_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O})$, one part of the salt in twenty parts of water.

PREPARATION—Mix a solution of oxalic acid with a slight excess of ammonia and evaporate.

TESTS—It forms with a soluble lime salt a *white* precipitate, CaC_2O_4 , insoluble in oxalic ($\text{H}_2\text{C}_2\text{O}_4$) or acetic ($\text{H}_2\text{C}_2\text{H}_3\text{O}_2$) acid; a very delicate reaction.

IMPURITIES—It may contain all the impurities of oxalic acid or of ammonia. It should leave no residue when ignited on platinum foil.

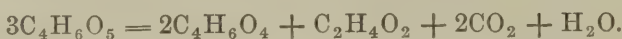
USES—It forms in neutral solutions very difficultly soluble compounds with Ca, Sr, Ba, and Pb, precipitating their corresponding oxalates. It is especially good for the detection and separation of calcium.

34. Ammonium succinate $((\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_4)$.

PREPARATION—Neutralize succinic acid with ammonia. The succinic acid is made by heating tartaric acid with phosphorus and iodine in the presence of water:



The succinic acid may be purified by dissolving in HNO_3 and recrystallizing. The most advantageous way of making succinic acid is by the fermentation of malic acid:



TESTS AND USES—It separates the sesquioxide of iron from other heavy metallic protoxides.

IMPURITIES—It may contain tartaric acid or hydriodic acid.

35. Ammonium sulphate $((\text{NH}_4)_2\text{SO}_4)$, one part of the salt to four parts of water.

PREPARATION—Neutralize sulphuric acid with ammonia and crystallize.

TESTS AND USES—Used in the separation of the alkaline earths. It precipitates Ba and Sr as sulphates.

IMPURITIES—It may contain the impurities of H_2SO_4 or NH_3 .

36. Ammonio-sulphate of copper.

PREPARATION—Made by adding NH_4HO , drop by drop, to a not too concentrated solution of CuSO_4 , until the precipitate at first produced is nearly redissolved; the clear solution to be employed.

37. Ammonio-nitrate of silver is made in the same way with AgNO_3 and NH_4HO .

TESTS AND USES FOR 36 AND 37—A solution of arsenious acid forms with 36 green CuHAsO_3 or $\text{Cu}_3(\text{AsO}_3)_2$, and with 37 forms yellow Ag_3AsO_3 , both soluble in NH_4HO and in dilute nitric acid.

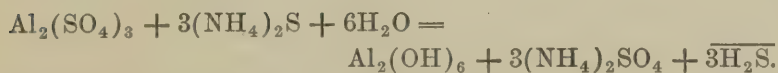
38. Ammonium sulphide— $(\text{NH}_4)_2\text{S}$ is colorless, and $(\text{NH}_4)_2\text{S}_2$ is yellow; the higher sulphides are red.

PREPARATION—Pass H_2S through NH_4HO until it does not produce a precipitate in a solution of MgSO_4 .

TESTS—All alkaline sulphides, even in very dilute solutions, give a *purple* coloration with nitro-prusside of sodium.

IMPURITIES—It should not contain any free ammonia (test by MgSO_4) nor ammonium carbonate (test by CaCl_2). It should leave no residue when evaporated to dryness and ignited. The solution spoils by long keeping.

USES—It is used as a group reagent. It precipitates as hydroxides Al and Cr from their solutions, with the escape of H_2S :



It precipitates the rest of the iron group, the lead group, and also, from acid solutions, the arsenic group as sulphides. Used in excess, it dissolves the sulphides of the arsenic group, and CuS to some extent. The phosphates of the alkaline earths and oxalates (except Mg) are precipitated unaltered; as calcium oxalate or phosphate, from a hydrochloric acid solution.

39. Barium acetate ($\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$). Keep in crystals.

PREPARATION—Dissolve barium carbonate in acetic acid, filter, and crystallize.

TESTS AND USES—To take the place of BaCl_2 in precipitating H_2SO_4 when it is desired to avoid the introduction of a chloride into the solution, or to convert the base into an acetate.

IMPURITIES—It may contain the impurities of acetic acid.

40. Barium carbonate (BaCO_3).

PREPARATION—Precipitate a hot solution of BaCl_2 with $(\text{NH}_4)_2\text{CO}_3$ mixed with some ammonia; wash the precipitate a number of times, and add water to the consistency of cream.

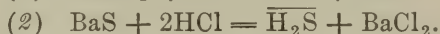
TESTS— H_2SO_4 evolves CO_2 , and precipitates the Ba *completely* as *white* BaSO_4 , insoluble in all dilute acids.

IMPURITIES—It may contain HCl and NH_3 .

USES—To separate Fe_2O_3 , Cr_2O_3 , and Al_2O_3 from MnO , ZnO , NiO , MgO , etc., in neutral solutions free from sulphates.

41. Barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$), one part of the salt in ten parts of water.

PREPARATION—It may be formed from witherite, BaCO_3 , by treatment with HCl , or from heavy spar, BaSO_4 , by fusing with C , thereby producing BaS , and subsequent treatment with HCl :



TESTS— H_2SO_4 gives a *white* precipitate of BaSO_4 , insoluble in acids. Test for chlorine as before described.

IMPURITIES—It should be neutral; H_2SO_4 must *completely* precipitate it.

USES—As a special test for H_2SO_4 and as a group reagent for acids.

42. Barium hydroxide ($\text{Ba}(\text{OH})_2$). A saturated aqueous solution at 15°C . contains one part in twenty.

PREPARATION—Fuse the carbonate (witherite) with powdered charcoal, and treat with water, or dissolve the oxide in water: $\text{BaO} + \text{H}_2\text{O} = \text{Ba}(\text{OH})_2$.

TESTS—Same as No. 41, for Ba.

USES—To precipitate magnesia, and in the detection and estimation of H_2SO_4 and CO_2 , especially in the atmosphere. and H_3PO_4 .

43. Barium nitrate ($\text{Ba}(\text{NO}_3)_2$), one part in fifteen parts of water.

PREPARATION—Treat BaCO_3 or BaO with dilute HNO_3 .

TESTS—Same as No. 41, for Ba.

IMPURITIES—May contain HCl .

USES—It can be used to take the place of BaCl_2 when it is desirable to avoid the presence of a metallic chloride in the fluid.

44. Barium peroxide (BaO_2).

PREPARATION—By heating BaO in a current of air or of oxygen.

TESTS AND USES—It is used to form hydrogen peroxide as follows: $\text{BaO}_2 + 2\text{HCl} = \text{BaCl}_2 + \text{H}_2\text{O}_2$.

IMPURITIES—It may contain BaO .

45. Bromine (Br), sp. gr. 2.96.

PREPARATION—By treating the “bittern” of salt works with chlorine.

TESTS—By the odor. By the *orange* color it gives to starch solutions. By giving with AgNO_3 a *yellowish white* precipitate of AgBr .

IMPURITIES—It may contain Cl .

USES—As an oxidizing agent. It will take the place of Cl in most cases.

46. Bromine water (water saturated with bromine). One part of bromine is soluble in thirty-four parts of water; sp. gr. 1.024; is used in preference to Br in some cases.

47. Calcium carbonate (CaCO_3).

PREPARATION—A hot solution of CaCl_2 is precipitated by $(\text{NH}_4)_2\text{CO}_3$, with the addition of some NH_4HO ; wash well with hot water, and dry thoroughly.

TESTS—Ammonium oxalate gives with a solution of calcium a *white* precipitate of CaC_2O_4 . Test CO_2 as before described.

IMPURITIES—May contain $\text{Ca}(\text{OH})_2$, HCl , and salts of the fixed alkalies.

USES—Used as a flux in the analysis of silicates when testing for the alkali metals.

48. Calcium chloride ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$), one part of the salt in eight parts of water.

PREPARATION—Marble is treated with hydrochloric acid:



The CaCl_2 is recrystallized.

TESTS—Ammonium oxalate gives a *white* precipitate of CaC_2O_4 . Test for Cl as before described.

IMPURITIES—It must have a neutral reaction, and not be colored nor precipitated by $(\text{NH}_4)_2\text{S}$.

USES—It is used as a group reagent for the acids, and in most cases acts like BaCl_2 . The anhydrous salt serves to dry gases, and for the absorption and estimation of water in organic analysis.

49. Calcium fluoride (CaF_2).

PREPARATION—It is found native as fluor spar sufficiently pure for use.

TESTS AND USES—When treated with H_2SO_4 , $\overline{\text{HF}}$ is liberated, which etches glass:



50. Calcium hydroxide ($\text{Ca}(\text{OH})_2$).

PREPARATION—Dissolve quicklime (CaO) in water. Use the clear solution; keep in a well stoppered bottle.

TESTS AND USES—To detect CO_2 , and to liberate NH_3 from ammonium salts. It separates tartaric acid from citric acid—by precipitating the former in the cold, and the latter on boiling. To effect the removal of H_2SO_4 and H_3PO_4 . It precipitates Magnesium from its solution as $\text{Mg}(\text{OH})_2$, nearly insoluble in water but soluble in NH_4Cl .

51. Calcium oxide (CaO), quicklime.

PREPARATION—The CaCO_3 is heated, when $\overline{\text{CO}}_2$ passes off.

TESTS AND USES—It is chiefly used to liberate ammonia from ammonium salts, and in making soda lime.

52. Calcium sulphate ($\text{CaSO}_4, 2\text{H}_2\text{O}$), gypsum.

PREPARATION—Dissolve gypsum in water; use a saturated aqueous solution.

TESTS AND USES—Used in the separation of the alkaline earths. CaSO_4 precipitates Ba *immediately*, Sr *after the lapse of some time*, and Ca *not at all*.

53. Carbon disulphide (CS_2), sp. gr. 1.27; boils at 45°C .

PREPARATION—Made by passing the vapor of sulphur over heated charcoal: $\text{C} + \text{S}_2 = \text{CS}_2$. It is nearly insoluble in water, but very soluble in alcohol and in ether.

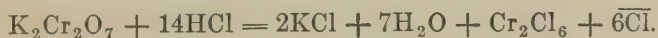
TESTS—The odor of its vapor is very offensive.

IMPURITIES—It may contain SO_2 , S, and H_2S .

USES—It is a solvent for sulphur, phosphorus, iodine, oils, gums, resins, and fats; also used for making thermometers for registering very low temperatures.

54. Chlorine water (water saturated with chlorine). Water absorbs at 10°C ., two and fifty-eight hundredths times its volume of chlorine. Keep in a cool place, in a bottle covered with paper.

PREPARATION—When a small quantity of chlorine is required, it can be made in a test tube as follows: Heat HCl with $\text{K}_2\text{Cr}_2\text{O}_7$ —



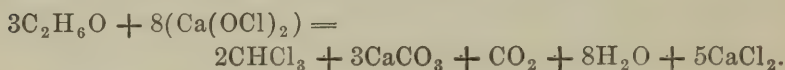
TESTS—Odor of chlorine.

IMPURITIES—May contain HCl and Cr_2Cl_6 .

USES—It possesses most of the properties of the gas. It is an oxidizing agent, and a solvent for Au and Pt.

55. Chloroform (CHCl_3), sp. gr. 1.48; boils at 61°C . (purified chloroform); chemically known as *trichlormethane*.

PREPARATION—Made by heating to 65°C ., ten parts of bleaching powder, forty parts of water, and one part of alcohol; sp. gr. .834. The following is thought to represent the reaction:



Wood spirit, *acetone*, oil of turpentine, and many essential oils, likewise yield chloroform when treated with chloride of lime. It is almost insoluble in water, but soluble in ether and alcohol.

TESTS—Heat a few drops of chloroform with aniline and alcoholic caustic soda solution; the *characteristic odor* of carbamine is observed. By this process one part of chloroform may be detected in six thousand parts of water.

IMPURITIES—It may contain H_2SO_4 , Na_2CO_3 , Cl , $\text{C}_2\text{H}_4\text{O}$, fusel oil, organic impurities, and water. It must have a neutral reaction, and leave no residue on evaporation.

USES—To remove Br and I from aqueous mixtures. It is a general solvent for gums, oils, and resins, and a group reagent for the alkaloids.

56. Cobalt nitrate ($\text{Co}(\text{NO}_3)_2$), one part of the salt to ten parts of water.

PREPARATION—Dissolve cobalt oxide in nitric acid, and recrystallize: $\text{Co}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$.

TESTS—With a borax bead it gives a *blue* color.

IMPURITIES—It may contain other metals, as Ni, and in some cases As.

USES—In the dry way for blowpipe use. It is a good test for Al, Zn, Si, Mg, and Sn.

57. Copper (Cu), metallic.

TESTS AND USES—It is employed to detect HNO_3 , also to detect Hg and As. It is used in the manufacture of SO_2 and NO, also in organic analysis of nitrogenous substances, to effect the reduction of the nitric oxide.

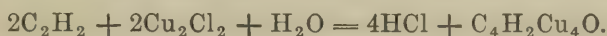
58. Cuprous chloride (Cu_2Cl_2), sp. gr. 3.7.

PREPARATION—Boil CuCl_2 with HCl and Cu filings; the solution yields, on the addition of water, a white precipitate of Cu_2Cl_2 .

TESTS—The HCl solution of Cu_2Cl_2 forms a compound having a mother of pearl lustre.

IMPURITIES—It may contain CuCl_2 .

USES—For absorbing CO in gas analysis ($\text{Cu}_2\text{Cl}_2\text{CO} + 2\text{H}_2\text{O}$). The ammoniacal solution of cuprous chloride gives with acetylene a *red* precipitate of di-acetylene cuprous oxide:



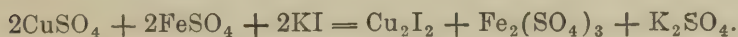
59. Copper sulphate ($\text{CuSO}_4, 5\text{H}_2\text{O}$), one part of the salt in eight parts of water.

PREPARATION—By treating pure Cu with H_2SO_4 .

TESTS—Ammonia gives a *blue* solution with Cu ; potassium ferrocyanide gives a *dark brown* precipitate of $\text{Cu}_2\text{FeC}_6\text{N}_6$. Potassium xanthate is the most delicate test for copper.

IMPURITIES—When precipitated by iron it always contains traces of it.

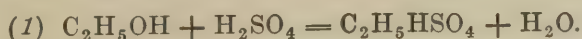
USES—To precipitate HI (when mixed with two and one-half parts of FeSO_4) as a *white* cuprous iodide, Cu_2I_2 , the only iodide of copper. The reaction of CuSO_4 with HI and KI are similar:



It is used to detect arsenious and arsenic acids, also as a delicate test for the soluble ferrocyanides.

60. Ether ($(\text{C}_2\text{H}_5)_2\text{O}$), commercial ether or ethyl oxide, sp. gr. .750. Contains 74 per cent. ether and 26 per cent. alcohol.

PREPARATION—By acting on alcohol with H_2SO_4 between 130° and $137^\circ \text{C}.$:



TESTS—The odor is characteristic. Ether, of the above specific gravity, dissolves in three and eight-tenths parts of water. *Absolute* ether forms a clear mixture with any proportion of oil of copaiba. *Anhydrous* ether forms a clear mixture with CS_2 ; if the smallest quantity of H_2O be present, the mixture is milky.

IMPURITIES—Alcohol, water, and sulphuric or sulphurous acids.

USES—It dissolves the resins, fats, sulphur, phosphorus, iodine, and ferric, mercuric, and auric chlorides.

61. Ferric chloride (Fe_2Cl_6), one part of the salt in fifteen parts of water. It should be as nearly neutral as is possible.

PREPARATION—Dissolve iron or iron oxide in HCl , and add a few drops of HNO_3 to oxidize it.

TESTS— $\text{K}_4\text{FeC}_6\text{N}_6$ gives a *blue* precipitate, $\text{Fe}_4(\text{FeC}_6\text{N}_6)_3$; KCNS gives a *blood red* color, $\text{Fe}(\text{CNS})_3$.

IMPURITIES—The ferrous salts.

USES—It is used in detecting the cyanides and phosphoric acid. It forms basic salts with benzoic, succinic, and acetic acids, which are completely precipitated from neutral solutions upon boiling. It gives characteristic colorations with free acetic, formic, and meconic acids, *red*; with salicylic acid, *violet*; with tannic acid, *black ink*; with phenol, creosote, daphnin, morphine, and pseudomorphine, *blue*.

62. Ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), the dry salt; also, solution, one part of the salt to ten parts of water.

PREPARATION—Take the ferrous sulphate residues in making H_2S , concentrate and filter while hot, and let it crystallize under a layer of alcohol.

TESTS—Ferrocyanides form Everitt's white, $\text{K}_2\text{Fe}(\text{FeC}_6\text{N}_6)$, and the ferricyanides form Turnbull's blue, $\text{Fe}_3(\text{FeC}_6\text{N}_6)_2$.

IMPURITIES—May contain ferric salts.

USES—As a test for free HNO_3 ; as a test for ferricyanides, and as a good reducing agent for the precipitation of metallic gold from its solutions.

63. Gold chloride (AuCl_3).

PREPARATION—Gold is dissolved in aqua regia, avoiding an excess of HNO_3 . Evaporate on the water bath to dryness, and dissolve in water; it should be neutral.

TESTS AND USES—It is used as a test for stannous salts, forming the “purple of Cassius.”

IMPURITIES—If made from gold coin, it may contain Cu.

64. Hydrogen (H).

PREPARATION—Made by the action of dilute H_2SO_4 on zinc— $\text{Zn} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2$. Add a drop of PtCl_4 when you want to hasten the process. Pass the H through a mercuric chloride solution, and then through a potash solution. If it is desired dry, pass it through H_2SO_4 or a CaCl_2 tube.

TESTS—When burned with O, water is formed.

IMPURITIES—Arsenic, hydrocarbons, and sometimes H_2S .

USES—To reduce oxides, chlorides, and sulphides to the metallic state, and also to protect certain bodies, such as metallic sulphides, from oxidation during ignition.

65. Indigo solution.

PREPARATION—Treat indigo with fuming sulphuric acid, added slowly, and in small portions at a time. Any considerable elevation of temperature must be avoided by placing the vessel in cold water.

USES—Used to fill prisms to cut off the sodium flame; also as tests for chlorine, and for chloric and nitric acids. A very dilute solution will in time decompose.

66. Iodine (I). It is purified by being resublimed.

USES—It is used in very many volumetric processes.

67. Lead acetate ($\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$), one part of the salt in ten parts of water.

PREPARATION—Dissolve lead oxide in acetic acid, using an excess of acid to prevent basic salts from forming:



Paper soaked in this solution is called *lead paper*. Dry, and keep in a well stoppered bottle.

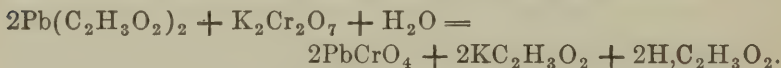
TESTS— H_2S precipitates Pb from its solutions as a *black* PbS ; $\text{K}_2\text{Cr}_2\text{O}_7$ precipitates *yellow* PbCrO_4 .

IMPURITIES—Generally contains basic salts of lead.

USES—It is used as a special test for certain elements and compounds, as H_2S , $\text{K}_2\text{Cr}_2\text{O}_7$, H_3PO_4 , $(\text{NH}_4)_2\text{S}$, and H_2SO_4 , and in the preparation of organic acids.

68. Lead chromate (PbCrO_4).

PREPARATION—Precipitate acetate of lead with potassium bichromate; wash, dry, and heat to a bright redness:



TESTS—It is insoluble in water. When fused on charcoal with sodium carbonate, Pb is obtained; in like manner the Cr can be oxidized and tested.

IMPURITIES—It may contain lead carbonate.

USES—For the combustion of organic substances. It is converted by heat into the sesquioxide of chromium and basic chromate of lead, and gives off O .

69. Litmus paper.

PREPARATION—Dissolve litmus in water, filter, and divide into two equal parts; saturate the free alkali in one by dilute H_2SO_4 until the color just appears red, and add the other part of the filtrate; draw strips of paper through the solution, and dry on threads. To make the *red litmus paper*, add H_2SO_4 until distinctly red, and treat as above described.

TESTS AND USES—The blue is used to detect the presence of acids; and the red, of alkalies, alkaline earths, alkaline carbonates, and the soluble salts of some weak acids.

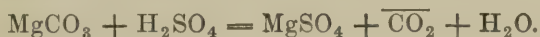
70. "Magnesium mixture."

PREPARATION — Dissolve one hundred and one and five-tenths grams of crystallized magnesium chloride, two hundred grams of ammonium chloride, and four hundred grams of ammonium hydroxide (sp. gr. 96), the whole made up to one liter with water. This amount will precipitate thirty-five and five-tenths grams of phosphoric acid.

TESTS AND USES — Used as a test for arsenic and phosphoric acids and their soluble salts.

71. Magnesium sulphate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), one part of the salt in ten parts of water.

PREPARATION — Made from the native carbonate by treating it with sulphuric acid:



Dolomite (CaMg_2CO_3) contains Ca, but it forms with H_2SO_4 an *insoluble* CaSO_4 , while the MgSO_4 is *very soluble*; the Mg can be separated in this way from the Ca.

TESTS AND USES — Used for the detection of phosphoric and arsenic acids, which it precipitates in the presence of NH_4HO and NH_4Cl as ammonium magnesium phosphate or arsenate, sparingly soluble. It is used to test the *complete* saturation of NH_4HO with H_2S in making $(\text{NH}_4)_2\text{S}$.

72. Mercury (Hg), sp. gr. 13.6.

PREPARATION — Cinnabar (HgS) is roasted in a suitable kiln: $\text{HgS} + \text{O}_2 = \text{Hg} + \overline{\text{SO}_2}$.

TESTS AND USES — At ordinary temperatures, the only liquid metal. Used in filling thermometers and barometers, and in gas analysis to collect dried gases. It is used to make sodium amalgam.

73. Mercuric chloride (HgCl_2), one part of the salt in sixteen parts of water.

PREPARATION — Dissolve Hg in aqua regia, and crystallize.

TESTS—KI forms with a solution of HgCl_2 a *red* precipitate of HgI_2 , soluble in an excess of either reagent.

IMPURITIES—It may contain the mercurous salts.

USES—As a test for tin (as stannous chloride), HI, and KI. Mercuric oxide, sulphide, iodide, iodate, basic carbonate, oxalate, phosphate, arseniate, arsenite, ferrocyanide, and tartrate are *insoluble* in water.

74. Mercurous nitrate ($\text{HgNO}_3, 2\text{H}_2\text{O}$).

PREPARATION—Dissolve one part of Hg in one part of HNO_3 (sp. gr. 1.2), and let the crystals separate; dissolve these in H_2O , mixed with dilute (one to sixteen of H_2O) HNO_3 , by trituration in a mortar; filter, and keep the filtrate in a bottle, with some Hg covering the bottom of the vessel.

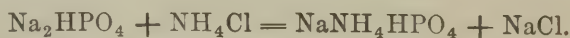
TESTS—It forms with KI a *greenish yellow* precipitate of Hg_2I_2 .

IMPURITIES—The *mercuric* salt.

USES—Mercurous compounds of ordinary occurrence are *insoluble* in water, except the normal nitrate. Fixed alkali hydroxides precipitate *black* Hg_2O , insoluble in alkalies. NH_4HO precipitates *black* $(\text{NH}_2\text{Hg}_2)\text{NO}_3$, insoluble in alkalies and soluble in acids. It serves as a test for many acids, as formic acid.

75. Microcosmic salt ($\text{NaNH}_4\text{HPO}_4, 4\text{H}_2\text{O}$), crystals.

PREPARATION—Add a hot solution of disodic hydric phosphate to ammonium chloride. Free the crystals from NaCl by recrystallization:



TESTS—The tests for phosphorus and for ammonia.

IMPURITIES—If it forms a clear colorless bead, the impurities may be disregarded.

USES—For the identification of SiO_2 by the blowpipe, and also to take the place of borax beads.

76. Millon's reagent.

PREPARATION—Dissolve one part of mercury in one part of HNO_3 (sp. gr. 1.42); dilute with twice its bulk of water, and filter after twenty-four hours.

TESTS AND USES—It is a good test for all "*protein*" bodies. When heated with albumin, etc., it produces first a yellow and afterwards a red coloration.

77. Oxygen (O).

PREPARATION—Made by heating a mixture of KClO_3 and MnO_2 as follows: $\text{KClO}_3 + \text{MnO}_2 = \text{MnO}_2 + \text{KCl} + \overline{\text{O}}_3$.

TESTS—A mixture of potassium hydroxide and pyrogallie acid absorbs oxygen and *blackens* the pyrogallate. When O is burned with H, water is formed.

IMPURITIES—Impurities can be removed by passing it through a solution of KHO (sp. gr. 1.27), then through U tubes containing soda lime, and then through U tubes containing CaCl_2 .

USES—As an oxidizing agent and in organic analysis in the place of CuO and PbCrO_4 .

78. Platinum vessels (care of). The following precautions must be observed in their use:

1. Never fuse caustic alkalies, alkaline earths, nor their nitrates in platinum. Use a *silver* dish instead.
2. Never fuse the alkaline sulphides with carbon, nor other fusible sulphides, nor cyanides in a platinum dish.
3. Easily fusible metals, or their oxides with carbon, form fusible alloys with Pt. Never fuse organic metallic salts in Pt.
4. Phosphates and carbon at a high temperature give rise to fusible phosphides of platinum.
5. Chlorine, bromine, aqua regia, or mixtures that liberate them, dissolve platinum.
6. Silicon, at high temperatures, combines with platinum.
7. Clean them by fusing in them bisulphate of potash or borax, and polish them with *fine* sea sand or emery flour, and *always* keep them polished. When fusing an unknown body on platinum foil, always do it on one corner, *never* in the center.

79. Platinum chloride ($\text{PtCl}_4, 10\text{H}_2\text{O}$), one part of the salt in ten parts of water.

PREPARATION—Dissolve *clean* platinum scraps in aqua regia, and evaporate on the water bath to dryness. The residue should dissolve completely in alcohol.

TESTS AND USES—It is a quantitative test for K, forming a *yellow* precipitate of $\underline{2\text{KCl}, \text{PtCl}_4}$; also a test for NH_4HO , Cs, and Ru.

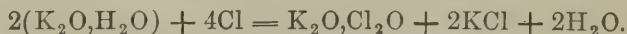
80. Potassium bisulphate (KHSO_4).

PREPARATION—As a bye product in the manufacture of HNO_3 ; also made by treating the normal sulphate with sulphuric acid.

TESTS AND USES—Used as an important reagent in the dry way for blowpipe work; also used for cleaning Pt crucibles.

81. Potassium chlorate (KClO_3), crystals.

PREPARATION—Pass a slow current of Cl into a cold dilute solution of KHO: (1) potassium chloride and potassium hypochlorite are formed—



(2) If this solution is boiled, it is converted into the chlorate and chloride— $3(\text{K}_2\text{O}, \text{Cl}_2\text{O}) = 4\text{KCl} + 2(\text{KClO}_3)$.

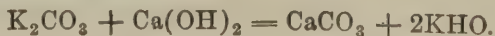
TESTS—When heated, oxygen is given off; K gives a violet tinge to a colorless flame.

IMPURITIES—KCl and Cl. It is sometimes made from $\text{CaO}, \text{Cl}_2\text{O}$, when it may contain calcium sulphate and chloride.

USES—As an oxidizing agent with HCl or H_2SO_4 , and in the manufacture of oxygen.

82. Potassium hydroxide (KHO), solid, and a solution of a specific gravity of 1.27.

PREPARATION—Made by treating carbonate of potash with milk of lime, as follows:

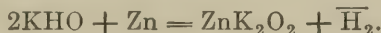


If the solution of potassium is too strong, the lime will not remove the whole of the carbonic acid. The CaCO_3 is *insoluble* and settles out; the liquid is evaporated in an iron or silver dish.

TESTS—It gives a *violet* flame, and is *strongly* alkaline.

IMPURITIES—It is hard to free it from carbonates. When KHO is dissolved in *absolute* alcohol, and the solution evaporated in a silver dish, the residue will be nearly pure KHO. *Pure* potassium hydroxide is very difficult to make; the above treatment will give a sufficiently pure product.

USES—It expels ammonia from its salts. A solution of a specific gravity of 1.27 (one of KHO to three of water) is used for the direct determination of CO_2 . It is used for the determination of sulphur in organic substances. It precipitates many oxides and hydroxides, some of which are *soluble* in an excess of KHO, as Al, Cr, and Pb; others are *insoluble* in excess, as Fe and Bi. It also dissolves some salts, as lead chromate and sulphur compounds. It is used to generate hydrogen by dissolving Zn, in contact with Fe or Pt:



83. Potassium iodide (KI), one part of the salt to twenty of water.

PREPARATION—Iodine is added to a solution of potassium hydroxide, forming an iodide and an iodate:



When KIO_3 is heated, it decomposes into $\text{KI} + \overline{\text{O}_3}$.

TESTS—Mercuric chloride gives a *red* precipitate of HgI_2 , soluble in an excess of either reagent, as follows:



IMPURITIES—It may contain an iodate, and the impurities of KHO and of I. When KI is dissolved in dilute H_2SO_4 , it should be colorless; a *brown* color indicates free iodine.

USES—It is used as a solvent for iodine, and in the estimation of free chlorine. It precipitates silver, mercurous and mercuric, lead, copper, bismuth, and cadmium salts from their solutions as iodides.

84. Potassium metantimoniate (KSbO_3). Dissolve when required, as it is not permanent in solution.

PREPARATION—Fuse antimonie acid with a large excess of potassium hydroxide; dissolve, filter, and digest hot in a silver dish, with an excess of potassium hydroxide; decant the alkaline liquor, and stir the residue until it becomes dry.

TESTS AND USES—It cannot be used in *acid* solutions. It produces in neutral or alkaline solutions of sodium a *white*, slow-forming, crystalline precipitate of NaSbO_3 that is nearly insoluble in cold water.

85. Potassium nitrate (KNO_3), the crystallized salt.

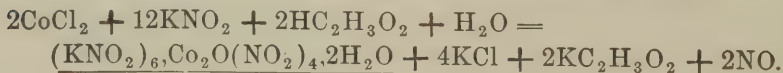
PREPARATION—It is found native in many hot countries. It is made by boiling together solutions of Chili saltpeter, and potassium chloride: $\text{NaNO}_3 + \text{KCl} = \text{KNO}_3 + \text{NaCl}$. The NaCl crystallizes out first. The mother liquor contains the KNO_3 .

TESTS AND USES—It is an oxidizing reagent.

86. Potassium nitrite (KNO_2), one part of the salt to two parts of water.

PREPARATION—By passing nitrous acid into KHO until it is completely saturated. The nitrous acid may be made by taking two parts of starch, eight parts of HNO_3 (commercial, sp. gr. 1.4), and eight parts of water, and heating; as soon as the action begins, the flame is taken away. The fumes (N_2O_3) are passed first into a cooled empty flask, and then into KHO .

TESTS AND USES—It serves in the presence of free acid to liberate iodine from its compounds. It detects and separates cobalt by precipitating it as potassium cobaltic nitrite:



87. Potassium sulphate (K_2SO_4), one part of the salt to two hundred parts of water.

PREPARATION—Purify the commercial salt by recrystallization, when it will be sufficiently pure.

TESTS AND USES—It serves to separate Ba from Sr (see No. 52). It is used in preference to H_2SO_4 , as it does not, like that reagent, disturb the neutrality of the solution.

88. Silver nitrate ($AgNO_3$), one part of the salt in thirty parts of water.

PREPARATION—Silver coin can be used in its preparation. The coin is dissolved in HNO_3 , forming the nitrates of copper and silver. Precipitate the silver by HCl as silver chloride ($AgCl$); the copper remains in solution, and can be poured off; wash the $AgCl$ until the wash water gives no traces of copper with ferrocyanide. Reduce the $AgCl$ to pure metallic silver by means of Zn and HCl, the nascent hydrogen combining with the chlorine of the $AgCl$ to form HCl, leaving the silver in a finely divided state. Wash and dissolve the silver in the smallest possible quantity of HNO_3 , and evaporate to dryness. It should be neutral to litmus.

TESTS—Hydrochloric acid completely precipitates it as *white* $AgCl$, insoluble in dilute HNO_3 , but soluble in NH_4HO .

IMPURITIES—Made as above described, it will contain no impurities.

USES—A group reagent for the acids, and a special test for HCl.

89. Sodium acetate ($NaC_2H_3O_2 \cdot 3H_2O$), one part of the salt in ten parts of water.

PREPARATION—Neutralize sodium carbonate with acetic acid, and crystallize.

TESTS—It gives the reactions for sodium and acetic acid before described.

IMPURITIES—It may contain the impurities of sodium carbonate or of acetic acid.

USES—Sodium acetate added in sufficient amount to solutions containing other acids, results in forming salts of these acids, leaving acetic acid as the only free acid. In the presence of this free acid, in not too large excess, Zn is precipitated by H_2S as ZnS ; Fe_2O_3 and Al_2O_3 as basic acetates upon continued boiling.

90. Sodium carbonate ($\text{Na}_2\text{CO}_3, 10\text{H}_2\text{O}$), the crystals, the perfectly dried salt, and a solution containing one part of the salt to eight parts of water.

PREPARATION—It is made by roasting salt cake with an equal weight of chalk and about half its weight of coal.

TESTS—It gives the tests for sodium and for carbonic acid.

IMPURITIES—It may contain SiO_2 , H_2SO_4 , HCl , Fe , H_3PO_4 , and As .

USES—In the dry way as a flux. When fused it decomposes sulphates, silicates, and arsenious sulphide. It is a special test in the dry way, when KNO_3 is added, for manganese and chromium, forming a *green* opaque bead of sodium manganate, or of *yellow* sodium chromate. It is used to saturate free acids. Its solution precipitates most of the metals as carbonates.

91. Sodium chloride (NaCl), crystals.

PREPARATION—Common salt is purified by passing into its concentrated solution, hydrochloric acid gas to saturation; the small crystals of NaCl which form are collected on a funnel, drained, and washed with HCl ; the NaCl is then dried in a porcelain dish until the HCl has been completely evaporated.

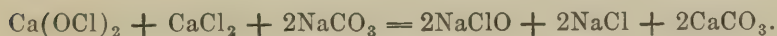
TESTS—It gives the tests for Na and Cl .

IMPURITIES—It may contain CaSO_4 and MgCl_2 .

USES—It is used for the volumetric assay of silver, and to standardize solutions of silver for the estimation of chlorine. It is usually fused before weighing; if the gas flame acts on the salt, HCl escapes, and sodium carbonate is formed.

92. Sodium hypochlorite (NaClO), the solution.

PREPARATION—(1) Hypochlorites are made by passing Cl through a solution of metallic hydroxides. (2) Agitate one part of good bleaching powder with ten parts of water; add sodium carbonate to the solution as long as a precipitate is formed, allowing the solid matter to subside, and use the supernatant liquid:



TESTS AND USES—It liberates iodine from KI . It is a good oxidizing agent. It dissolves arsenic spots by oxidation to arsenic acid, distinction from antimony.

93. Soda lime.

PREPARATION—To a solution of sodium hydroxide add twice the weight of the best quicklime, and evaporate to dryness in an iron vessel; heat to a low red heat in an iron or Hessian crucible, and break up the lumps in an iron mortar, passing them through a coarse sieve—eight meshes to an inch.

TESTS AND USES—It should be free from ammonia, and effervesce but slightly with dilute HCl . It is used as an absorbent for carbonic acid, and in the analysis of nitrogenous organic substances.

94. Sodium nitrate (NaNO_3), crystals.

PREPARATION—Neutralize sodium carbonate with nitric acid, evaporate, and crystallize. It is found native in an impure state (Chili saltpeter).

TESTS AND USES—It is a powerful oxidizing agent. It is used to convert the sulphides of tin, arsenic, and antimony into oxides or acids; also to complete the combustion of organic substances.

95. Sodium nitroprusside ($\text{Na}_4\text{C}_{10}\text{N}_{10}\text{N}_2\text{O}_2\text{Fe}_2, 4\text{H}_2\text{O}$), one part of the salt in twenty parts of water.

PREPARATION—Digest one part of potassium ferrocyanide with two parts of HNO_3 and two parts of water until it ceases to produce a blue precipitate with iron salts; when cool, neutralize the mother liquid with sodium carbonate, and then collect the red crystals.

TESTS AND USES—It gives with the alkaline sulphides a *purple* color; a very delicate test.

96. Sodium palladio-chloride ($\text{PdCl}_4 \cdot 2\text{NaCl}$), one part of the salt in ten parts of water.

PREPARATION—Dissolve five parts of palladium in aqua regia, add six parts of sodium chloride, and evaporate in a water bath to dryness.

TESTS AND USES—The brownish solution is a good reagent for detecting and separating iodine from Br and Cl.

97. Sodium ammonium phosphate ($\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$), or microcosmic salt.

PREPARATION—Heat six parts of disodium phosphate and one part of pure ammonium chloride with two parts of water; free from the NaCl by recrystallization and by the addition of ammonia; dry the purified crystals, and pulverize.

TESTS AND USES—When heated, it first loses its water, then its ammonia, and becomes a glassy, transparent mass of sodium metaphosphate, NaPO_3 , which dissolves many metallic oxides with characteristic colors. In the dry way, it is used for beads; it is a special test for the determination of silica.

98. Sodium sulphite (Na_2SO_3) and **acid sodium sulphite** (NaHSO_3), one part of the salt to five parts of water.

PREPARATION—Made by passing SO_2 over crystals of Na_2CO_3 until the evolution of CO_2 ceases.

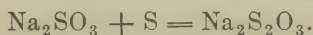
TESTS—Lead acetate precipitates white lead sulphite, PbSO_3 , easily soluble in dilute nitric acid, and not blackening when boiled (distinction from thiosulphate).

IMPURITIES—It may contain sodium sulphate.

USES—It is a good *reducing* agent in acid liquids, changing arsenic acid to arsenious acid, chromic acid to chromic oxide, and ferric oxide to ferrous oxide. It separates arsenious sulphide, which is soluble in it, from the sulphides of antimony and tin, which are insoluble in it.

99. Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), or sodium hyposulphite, one part of the salt in forty parts of water.

PREPARATION—Treat a solution of Na_2SO_3 with sulphur:



TESTS AND USES—It gives a precipitate of S, with evolution of SO_2 , when its solutions are treated with HCl ; it has great reducing power, and does not precipitate calcium (distinction from sulphite). It is employed in volumetric analysis. It separates Sn from As and Sb by precipitating, from acid solutions, As and Sb as sulphides. It is a solvent for several salts, as AgCl , Hg_2Cl_2 , and CaSO_4 .

100. Stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), one part of the salt in six parts of water, acidulated with HCl .

PREPARATION—Dissolve tin in hydrochloric acid, having an excess of tin in the vessel; keep the solution in a well stoppered bottle containing small pieces of tin.

TESTS AND USES—It is a good *reducing* agent, and a special test for mercury and gold.

101. Starch solution.

PREPARATION—Pulverize a piece of starch the size of a pea in a mortar, and add water enough to wash it out; this is added to a quart of boiling water, and the boiling is continued for two minutes; use when *cold*. Starch paper is made by saturating unsized paper in this liquid and drying it.

TESTS AND USES—Used as a test for free iodine, with which it gives a blue color.

102. Turmeric paper.

PREPARATION—Heat one part of bruised turmeric root with six parts of weak alcohol; filter the tincture obtained, and steep slips of unsized paper in the filtrate; they acquire a yellow tint.

TESTS AND USES—It is used as a test for the alkalies and for boracic acid. Mix an alkaline borate with HCl to slight acid reaction; a slip of turmeric paper is dipped into it and then dried at 100° C., the dipped portion will show a peculiar wine red tint; this reaction is very delicate.

103. Zinc (Zn), granulated metal.

PREPARATION—Melt Zn in an iron ladle, and pour in a small stream from a height of six feet into a jar of cold water, and dry. Chemically pure Zn is used in Marsh's test. Zinc free from iron is used in volumetric analysis of iron. For ordinary use, zinc free from arsenic is all that is required.

TESTS AND USES—To generate hydrogen, and for arsenetted and antimonetted hydrogen. It precipitates the less electro-positive metals from their solutions, as Cu. It is used to detect sulphurous acid and phosphorous acid.

It is a very valuable exercise for the student to make the reagents, as a laboratory practice, *and to always test their purity*. In all his work, he must bear this thought in mind, "Trifles make perfection, but perfection is no trifle."

CHAPTER II.

TESTS IN THE DRY WAY.

104. The following hints will be of use to the student:

1. Have everything neat and clean.
2. Never put anything away dirty.
3. Take the smallest possible quantity of the assay.
4. Know *what* you do, and *why* you do it.
5. Do the work *yourself*.
6. Note the characteristic tests, and remember two of them.
7. Look up the properties and reactions of the substance in some work of reference.
8. Never quit a substance until you have mastered it.
9. It is not *how much* you do, but *how well* you do it.
10. CAUTION — Do not expose yourself nor others needlessly to the vapors of the laboratory; as, chlorine, hydrogen sulphide, arsenic, etc.; the bad effects may not be perceptible immediately.

Keep accurate notes *at the time*. The following is the most convenient way to keep a note book:

NAME	SYMBOL	STATE	REACTION	REMARKS
(1) Sodium chloride.	NaCl.	White crystalline solid, in cubes.	Decrepitates; can be prevented by being finely pulverized.	The decrepitation is caused by the water mechanically inclosed in the crystals.
(2) Potassium chlorate.	KClO ₃ .	White crystalline solid, in monoclinic tables	Gives off oxygen: $\text{KClO}_3 = \text{KCl} + \overline{\text{O}_3}$.	It deflagrates upon a glowing coal, gives a violet flame.

The above can occupy two pages of a note book.

105. Note the physical properties of the substance—its state, solid or liquid.

If liquid, evaporate a portion to dryness, and use it in the following tests. (H_2O , H_2O_2 , the volatile acids, HCl , HNO_3 , $\text{HC}_2\text{H}_3\text{O}_2$, and many organic compounds will leave no residue).

If solid, or when rendered solid by evaporation, carefully note its form, crystalline or amorphous, compact or pulverulent, homogeneous, or an evident mixture; also its color, luster, feel, hardness, specific gravity, and sometimes its taste.

If it suffers any change upon exposure to the air, stable, deliquescent, or efflorescent.

106. Heat the dry and finely pulverized solid in a small glass tube open at one end (a matrass), at first gently, gradually increasing the heat as seems to be required, noting any changes that occur.

	INDICATION OF
<i>It decrepitates from H_2O mechanically inclosed in the crystalline mass.</i>	Haloid salts, as NaCl , etc.
<i>It becomes strongly luminous or phosphorescent.</i>	Alkaline earths, fluorides, etc.
<i>It changes color from—</i>	
<i>White to</i> { <i>yellow, on cooling is again white.</i> <i>dark yellow, “ yellowish . .</i> <i>dark yellow, on cooling is yellow-</i> <i>ish, fusible at red heat.</i> <i>reddish yellow, on cooling is red-</i> <i>dish yellow, fusible at a white</i> <i>heat</i>	Zinc, ZnO . Tin, SnO , TiO_2 . Bismuth, Bi_2O_3 . Cadmium, CdO . Lead, PbO .
<i>Green or reddish to nearly black, on cooling is reddish brown (magnetic).</i>	Iron, Fe_2O_3 .
<i>Red to brown, while hot, and on cooling is red, or becomes so on rubbing.</i>	Mercury, HgO .
<i>The red salts of Co, the pink salts of Mn, the blue and green salts of Cu and of Ni, lose H_2O, and at greater heat decompose, evolving acid vapors, and leaving dark colored oxides of.</i>	Co, Mn, Ni, and Cu.

		INDICATION OF
<i>Organic compounds</i> generally blacken from separation of carbon, evolving inflammable products like acetone ($\text{CO}(\text{CH}_3)_2$), and the odor of burnt sugar (C deflagrates with KClO_3).....		Acetates, tartrates, citrates, etc.
Alkaline salts of organic acids leave residues of carbonates, which effervesce with HCl: <i>It fuses quietly</i> , and on cooling again becomes solid without being decomposed.....		Some compounds of the alkalies.
<i>It gives off aqueous vapor</i> , that condenses in upper cool part of tube (test by litmus paper):		
(1) <i>A neutral reaction</i>		Hydrates, hydrous silicates.
Water of crystallization, the mass remains fluid while hot.....		Phosphates and Borates.
Water of crystallization, the mass becomes again dry.....		Alums, CuSO_4 , etc.
(2) <i>An acid reaction</i> , salts with weak bases like Al or Zn.....		Acid sulphates, fluorides.
(3) <i>An alkaline reaction</i> , as NH_3		NH_4 compounds.
<i>It yields a sublimate which is</i>		
White	without fusing, yellow when hot, Hg_2Cl_2 , with KHO becomes black.....	Hg. See below.
	melting at 205°C ., boiling at 295°C ., HgCl_2 , with KHO becomes yellow.....	Hg salts, heated with dry $\text{Na}_2\text{CO}_3 + \text{C}$ yield globules of metallic Hg.
	volatile at 165°C ., in slender needles, $\text{H}_2\text{C}_2\text{O}_4$, with H_2SO_4 evolves CO and CO_2	Oxalates; CO burns with a blue flame, and CO_2 renders $\text{Ca}(\text{OH})_2$ turbid.
	volatile at 218°C ., forms octahedral crystals, As_2O_3 , with H_2S becomes yellow.....	As, heated with C, gives garlic odor.
	heavy fumes, crystalline needles, Sb_2O_3 , with H_2S changes to orange.....	Sb_2O_3 , which is soluble in $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$.
	easily volatilized, in crystalline needles, NH_4 salts, with soda lime evolves NH_3	NH_3 , will brown turmeric paper.
	melts, but volatilizes with difficulty, and on cooling forms a transparent mass.....	PbCl_2 , blackens with H_2S .

		INDICATION OF
<i>Yellow needles</i> , fusible to red drops, becoming yellow on cooling, but on rubbing again become red.....		HgI ₂ .
<i>Yellow drops</i> , yielding dark red or even black drops when hot....		Sulpharsenides, As ₂ S ₂ .
<i>Red drops</i> , yielding dark red or even black drops when hot.....		Sulpharsenides, As ₂ S ₃ .
<i>Black drops</i> , both when hot and cold, but becoming red upon rubbing.....		HgS.
<i>Lustrous mirror</i>	{ black and compact, As..	Arsenides, As.
	{ formed of globules, Hg..	HgO, amalgams.
	{ with violet vapor of I...	I ₂ O ₅ , some iodides.
The mass after melting seems to boil, giving off a gas:		
<i>Condensable</i>	{ violet fumes of I, which change starch blue.....	Iodates and some iodides.
	{ red fumes of Br, which change starch yellow....	Bromates.
	{ colorless vapors of As and S, condensing to red or yellow drops.....	Sulpharsenides and persulphides.
<i>Odorous</i>	{ of burning sulphur = SO ₂ , which bleaches KMnO ₄ and K ₂ Cr ₂ O ₇ + H ₂ SO ₄ to green.	Note the odor.
	{ of peach kernels = CN, which burns with a rose colored flame, and changes AgNO ₃ to AgCN.....	Sulphites, sulphates, etc.
	{ of rotten eggs = H ₂ S, which blackens lead paper.....	Cyanogen compounds.
	{ of ammonia = NH ₃ , which blackens Hg ₂ Cl ₂	Hydrous sulphides and hyposulphites.
	{ of chlorine = Cl or Cl ₂ O, which turns starch paper + KI blue.....	Organic compounds, NH ₄ compounds, and cyanides.
	{ of acetone = CO(CH ₃) ₂ , is inflammable; the assay heated with H ₂ SO ₄ + C ₂ H ₆ O yields acetic ether.....	Hypochlorites, PtCl ₄ , and AuCl ₃ .
	{ odor of frankincense.....	Acetates.
	{ fumes which cause violent coughing.....	Benzoic acid.
	{ red fumes, soluble in H ₂ O....	Succinic acid.
		Nitrates and bromates.

		INDICATION OF
<i>Colorless and inodorous.</i>	ignites a glowing splinter, O, or N ₂ O from the salts of	I ₂ O ₅ , N ₂ O ₅ , NH ₄ NO ₃ , and peroxides.
	renders Ca(OH) ₂ turbid, CO ₂ ; burns with a blue flame, CO; both are better shown after adding H ₂ SO ₄ to assay.....	Formates and oxalates.

107. Heat the dry substance, together with certain dry reagents, in the matrass.

		INDICATION OF
<i>Oxidizing</i>	with KClO ₃ + Na ₂ CO ₃ (better on Pt foil); green indicates Mn; yellow, Cr.....	Mn and Cr.
<i>H₂S reaction</i>	with Na ₂ S ₂ O ₃ ; Zn white, Cd and As yellow, Mn and Cr green, Sb red, and Sn brown.....	Pb, Ag, Hg, Cu, Bi, Ni, Co, and Fe, black.
<i>H₂SO₄ reaction</i>	with KHSO ₄ decomposes formates, acetates, oxalates, also fluorides, etc..	Liberating these acids.
	with KHSO ₄ + MnO ₂ , evolving from the haloid salts, Cl, Br, and I.....	Haloid salts.
<i>Reducing</i>	with black flux (Na ₂ CO ₃ + C) or Na ₂ CO ₃ + KCN, the volatile elements	As, Hg.
	in tubes of very thin glass, with Mg wire or Na pellets, heat the dried solid, phosphides changed from phosphates + H ₂ O, evolve odor of decaying fish = PH ₃ ...	Phosphates.
	sulphides obtained from sulphates + H ₂ O or HCl on Ag, give black stain	Sulphur compounds.

108. Oxidize the substance by heating in a dry glass tube, open at both ends.

		INDICATION OF
<i>Evolves</i>	a whitish yellow sublimate, with fumes of burning sulphur = SO_2 .	Sulphides.
	a white to steel gray or red sublimate, odor of horse radish = SeO_2 .	Selenides.
	white fumes, fusible to colored drops = TeO_2	Tellurides.
	As_2S_3 oxidizes to As_2O_3 and SO_2 ; a portion sublimes in reddish yellow drops.....	Higher arsenides, except those of Ni and Co.
	colorless vapors of As_2O_3 , condenses in beautiful octahedral crystals, and on C gives a garlic odor.....	Higher arsenides, except those of Ni and Co.
	white dense fumes of Sb_2O_3 , sometimes accompanied by red drops of Sb_2S_3	Antimony compounds.
	amalgams and HgO yield Hg easily,	Mercury compounds.
	When strongly treated, the salts of Bi, Pb, and Sn yield yellowish white sublimates, Cd brown, Zn and Th white, better shown in film reactions.	

109. Confirm the most important of these reactions by repeating these tests, and by others in addition.

Remember—

All NH_4 salts when heated with soda lime yield NH_3 gas; test by litmus, HgCl_2 , and odor.

All S compounds fused with Na_2CO_3 yield a hepar, which with H_2O blackens Ag.

All Hg compounds fused with $\text{Na}_2\text{CO}_3 + \text{C}$ (black flux) yield globules of Hg.

All As compounds heated with C are reduced to As, and yield lustrous mirror. Note the garlic odor.

All Sb compounds fused with $\text{Na}_2\text{CO}_3 + \text{KCN}$ yield metallic Sb, oxidizable to white Sb_2O_3 .

These reactions are also valuable for the detection of the volatile acids, as HCl , HNO_3 , H_2CO_3 , $\text{HC}_2\text{H}_3\text{O}_2$, and also such as can be liberated by H_2SO_4 , as HCl , HBr , HI , etc.; also for H_2SO_4 and H_3PO_4 .

110. Heat a portion of the substance on charcoal before the blowpipe, first alone in the *oxidizing flame*.

	INDICATION OF
<i>It decrepitates</i>	NaCl or calcite.
<i>It deflagrates</i> —	
The residue is neutral to litmus paper....	Nitrates, chlorates, iodates.
The residue is alkaline to litmus paper...	Nitrates and carbonates of alkalies, alkaline earths.
<i>It fuses</i> —Sinks into the charcoal or forms—	
A crystalline bead.....	$Pb_3(PO_4)_2$.
A transparent mass. Test for alkaline reaction.....	Salts of alkalies, alkaline earths.
<i>It evolves an odor</i> —	
Of ammonia.....	NH_4 salts, some cyanides.
Of burning sulphur.....	Sulphides, hyposulphites.
Of garlic.....	As.
Of decaying horse radish.....	Se, Te.
<i>Yields fumes which form a coating on the coal:</i>	
<i>Easily volatilized</i> —White to bluish white,	
White, in R. F., garlic odor.....	As.
Dark gray, horse radish odor.....	Se.
Dark yellow.....	Te.
White.....	Sb.
Not included in the list are some other substances, as.....	Hg_2Cl_2 , NH_4Cl , and some sulphides.
<i>Not volatile in the O. F.</i> —	
light yellow.....	PbO dark yellow.
yellowish white.....	Bi_2O_3 orange yellow.
orange yellow.....	CdO reddish brown.
white, metal burns with a lurid flame.....	ZnO yellowish white.
white, coating unchanged by R. F.....	SnO pale yellow.
reddish brown, obtained only in a strong O. F....	AgO reddish brown.
dark yellow.....	PbO.
orange yellow.....	Bi_2O_3 .
reddish brown.....	CdO.
yellow.....	ZnO.
pale yellow.....	SnO.
reddish brown.....	AgO.

		INDICATION OF
<i>Leaves an infusible residue; oxidize thoroughly; this residue, moistened with $\text{Co}(\text{NO}_3)_2$, and again ignited, becomes after heating</i>		
<i>White and luminous..</i>	a blue infusible mass.....	Al_2O_3 , SiO_2 .
	a blue glass.....	Alkaline silicates, borates, and phosphates.
	a green mass.....	SnO , bluish; ZnO and TiO_2 , yellowish; Sb.
	a pink mass.....	MgO , TaO .
	a brown red mass.....	BaO .
<i>Colored</i>	a gray mass.....	CaO , SrO , Cr_2O_3 , Sb_2O_5 .
	Some of the residues yield characteristic borax beads..	CuO , CoO , Fe_2O_3 , MnO_2 , NiO , and Cr_2O_3 .
	Mn and Cr may also be tested by heating on Pt foil with KNO_3	Mn gives green mass + $\text{H}\bar{\text{A}}$ = red; Cr gives yellow mass (test by $\text{Pb}(\bar{\text{A}})_2$).
<i>Yields a characteristic color to the flame—</i> (Easily reducible metals are best tested on charcoal; and easily volatilized substances on Pt wire.) Moisten insoluble salt with strong HCl .		
<i>Yellow</i>		Na.
<i>Violet</i>		K, Rb, Cs, In.
<i>Red</i>	carmine.....	Li.
	crimson.....	Sr.
	mixed with yellow, after intense heating and moistening in hydrochloric acid.....	Ca.
<i>Green</i>	emerald green.....	Cu, Th.
	bluish green if Se is present....	Te.
	pale green to yellowish green....	Ba.
	yellowish green, moisten salts with strong H_2SO_4	B.
<i>Blue</i>	bluish green.....	P.
	azure blue.....	Se, Pb.
	azure blue, then green.....	CuCl_2 .
	light blue in R. F.....	As.
	faint, greenish blue.....	Sb.

111. Heat a portion of the substance, finely pulverized and mixed with Na_2CO_3 or KCN , in the reducing flame.

	INDICATION OF
<i>Evolves garlic odor</i>	As.
<i>Hepar is produced</i> , which, when moistened with H_2O or dilute HCl , blackens a silver coin.	S, Se, Te.
<i>Yields a volatile metal</i> , which immediately oxidizes and forms—	
A white coating on the coal; garlic odor.	As.
A coating, yellow when hot; white when cold.....	Zn, Te.
A coating, reddish brown, and easily volatilized.....	Cd.
<i>Yields a reguline metal</i> —	
<i>Malleable bead with incrustation</i> —	
Yellow to red.....	Pb.
Yellow.....	Tl.
White.....	In.
<i>Malleable bead with slight incrustation</i> —	
White, best with KCN	Sn.
Reddish.....	Ag.
<i>Brittle bead with incrustation</i> —	
White, easily volatilized.....	Sb.
Orange to yellow.....	Bi.
<i>Malleable scales or infusible powder</i> —	
Red, when rubbed on a hard surface..	Cu.
Yellow when rubbed....	Au.
Magnetic.....	Fe, Co, Ni.
Non-magnetic.....	Pt, Ir, Mo, W.

112. Heat a portion of the substance in the reducing flame, on a wood splinter coated with Na_2CO_3 , and charred; some metals are reduced. Wash away the Na_2CO_3 in a mortar, and test further.

	INDICATION OF
<i>Magnetic powders are</i>	Fe, Co, Ni.
<i>Malleable particles are</i>	Pb, Ag, Sn, Au.
<i>Brittle beads or spangles are</i>	Sb, Bi, Cu, Tl.

113. Bring the washed residues of Nos. 111 and 112 on a slip of glass, dissolve in HNO_3 , HCl , or aqua regia, and test.

HNO₃ solution—

Fe(NO₃)₃ gives a *blue* precipitate with K₄FeC₆N₆, red solution with KCNS.

Ni(NO₃)₂ gives a *green* precipitate with NaHO, which blackens with Br fumes.

AgNO₃ gives a *white* precipitate with HCl, soluble in NH₄HO, and a *red* precipitate with K₂Cr₂O₇.

Pb(NO₃)₂ gives a *white* precipitate with HCl and H₂SO₄, and a *yellow* precipitate with K₂Cr₂O₇.

Cu(NO₃)₂ gives a *red* precipitate with K₄FeC₆N₆, blue solution with NH₄HO.

HCl solution—

BiCl₃ gives a *white* precipitate with H₂O, which blackens with H₂S.

CoCl₂ solution is blue when warm, red when cold; test by borax bead.

SnCl₂ reduces AuCl₃ and HgCl₂; gives with borax bead and a trace of Cu, red Cu₂O.

Aqua regia solution

AuCl₃, reduced by SnCl₂ or FeSO₄ to a purplish powder.

PtCl₄ with NH₄Cl gives a *yellow* precipitate; ignited gives spongy Pt.

SbCl₃ gives a *white* precipitate with H₂O, soluble in H₂C₄H₄O₆, becomes orange with H₂S.

NOTE—Some of these reactions are especially useful—

The deflagration produced by the nitrates and chlorates.

The odor of As, Se, and S.

The non-volatile coatings of Pb, Bi, Zn, and Cd.

The coloration by cobalt of Al, Mg, Zn, and Sn.

The flame coloration of Na, K, Li, Sr, Cu, B, and Ba.

The hepar of S and Se.

The reguline metals of 111 and 112, with their confirmatory tests.

114. Put the substance in a small test tube, and add HCl and a thin strip of Zn. If a reduction follows,

It may color the liquid

Violet, indicates TiO₂.

Blue, indicates WO₃ or V₂O₅, changing finally to brown Mo, Ta, Nb.

Green, indicates CrO₃; in large excess also Fe₂O₃.

It may leave a deposit on Zn

Black, indicates Pt, Pd, Bi, Sb, Sn, Pb, Cd, Tl.

Brown to yellow, indicates Au, red Cu.

Brown to gray, indicates Ag, Hg, As, in dilute solutions the others also; repeat for "Reinsch's test" the Hg, As; Sb and Bi with a bright copper strip; heat the mixture, and afterwards heat coated strip in tube open at both ends.

It may evolve a gas

Due only to the HCl; to HCN, cyanides; to CO_2 , carbonates; to SO_2 , sulphites or hyposulphites, H_2S , sulphides.

Due also to the reducing action of nascent H; H_2S , H_2Se , H_2Te , H_3P , H_3As , H_3Sb ; test by paper moistened with $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, AgNO_3 , AuCl_3 ; reactions of the hyposulphites indicate compounds of P, As, and Sb.

115. It is well for the student to notice that—

The closed tube is used for detecting bodies that change color when heated, as Zn, O, and organic compounds, etc.; those that give off odors, as acetates, tartrates, etc.; those that are easily volatile, and yield a sublimate, as Hg, As, I compounds, etc.; those that seem to boil and give off a gas, as O, CO, CO_2 , etc.; those that are easily oxidized or reduced with dry reagents, as Pb, As, and Hg compounds.

The bent opened tube is used for easily oxidized substances, as sulphides, Sb compounds, As and Hg, etc.

Charcoal is used for detecting bodies that decrepitate, as NaCl; that deflagrate, as nitrates, etc.; that evolve an odor, as NH_3 and As; that yield coating on the coal, as Pb, Bi, etc.; that yield an infusible and colored residue when it has been treated with $\text{Co}(\text{NO}_3)_2$, as Mg, etc.; that yield easily reducible metals, as Pb, etc.

Platinum wire is used for easily volatile substances that color the flame, as K, Sr, etc.

A modification of the film tests (116) is made by using thin tablets of plaster-of-Paris and an alcoholic solution of iodine. The substance is placed on the tablet, moistened with the solution of iodine, and the blue flame is used, when the volatilized iodides are deposited on the cold surface; when suitably inclined, the reactions are similar to the film tests.

116. Beads of Borax and of Microcosmic Salt. For directions see page 64.

COLOR OF THE BEADS	WITH PHOSPHORUS SALT		WITH BORAX	
	OXIDIZING FLAME	REDUCING FLAME	OXIDIZING FLAME	REDUCING FLAME
Yellow to brown.	Fe, Ni, U, Ag, Va, Ce.	Fe, Ti.	Fe, U, Pb, Bi, Sb, Va.	Ti, W, Va, Mo, hot.
Red.	Fe, Ce, Ni, Cr, when hot and strongly saturated.	Cu, Fe, Ti, W, containing Fe (blood red) when hot.	Ce, Fe, Ni, when cold (reddish brown).	Cu strongly saturated (opaque).
(Amethyst.) Violet.	Mn, D, hot and cold.	Ti, Nb, cold, strongly saturated.	Mn, D, Co added to Ni, hot and cold.	Ti, cold.
Blue.	Co, Cu, hot and cold.	Co, W, Nb, hot and cold, strongly saturated.	Co, hot and cold. Cu, cold.	Co, hot and cold.
Green.	Cu, Mo, Co or Cu added to Fe, hot. Cr, U, cold.	Cr, U, Mo, Va, cold.	Cr, Va, cold. Cu, Co or Cu added to Fe, hot.	Fe, U, Cr, Va, hot and cold.
Gray.		Ag, Zn, Cd, Pb, Bi, Sb, Te, Ni, from reduced metal.		As with phosphorus salt; also Nb.
Colorless.	SiO ₂ , skeleton bead. Al, Sn, Ta, Nb, W, Zn, Cd, Pb, Bi, Sb, yellowish.	SiO ₂ , skeleton bead. Al, alkaline earths, Ce, D, Mn, Sn, not clear.	SiO ₂ , Al, Sn, not clear. Alkaline earths, Ag, Ta, Nb, Te, Ti, W, Zn, Cd, Pb, Bi, Sb.	SiO ₂ , Al, Sn, not clear. Alkaline earths, La, Ce, Ta, Mn, D, Cu.

NOTE.—Reduction takes place more easily with phosphorus salt (reduction is aided by addition of Sn); in general, the behavior of the various bodies is quite similar with borax and phosphorus. Salt of phosphorus is especially good for the detection of *silica*.

117. Film tests. For explanation see page 64.

TESTS IN THE DRY WAY.

63

NAME	OXIDE INCRUSTATION WITH AgNO_3 AND NH_3	IODIDE INCRUSTATION AND COATING	IODIDE INCRUSTATION WITH NH_3 BLOWN UPON IT	SULPHIDE INCRUSTATION AND COATING	SULPHIDE INCRUSTATION WITH $(\text{NH}_4)_2\text{S}$	METALLIC INCRUSTATION AND COATING
Sb.	Black, insoluble in NH_3 .	Orange; breathed upon, disappears for a time.	Disappears permanently.	Orange.	Disappears for a time.	Black, with brown coating.
As.	Lemon yellow or brownish red; soluble in NH_3 .	Orange yellow; when breathed upon, disappears for a time.	Disappears permanently.	Lemon yellow.	Disappears for a time.	Black, with brown coating.
Bi.	White.	Bluish brown, with a light red coating; if breathed upon, disappears for a time.	Rose red to orange yellow; chestnut brown when dry.	Umber brown, with a coffee brown coating.	Does not disappear.	Black, with soot-brown coating.
Hg.		Carmine and lemon yellow, breathed upon, does not disappear.	Disappears for a time.	Black.	Does not disappear.	Gray, incoherent coating.
Pb.	White.	Orange yellow to lemon yellow; breathed upon does not disappear.	Disappears for a time.	Through brownish red to black.	Does not disappear.	Black, with brown coating.
Cd.	Coating becomes blue black.	White.	White.	Lemon yellow.	Does not disappear.	Black, with brown coating.
Zn.	White.	White.	White.	White.	Does not disappear.	Black, with brown coating.

DIRECTIONS FOR BEADS—A small Pt wire is fused into a glass tube or rod, and the end heated, and dipped into anhydrous borax or salt of phosphorus, and heated to a colorless bead. The substance to be tested is touched by the hot bead, and a portion taken up, and heated in the oxidizing and then in the reducing flame. The chemistry of the process is quite simple. The metallic oxides are dissolved in the bead, and a colored glass forms; of course, the color will vary with the amount of the substance taken. Certain bodies, as the alkaline earths, dissolve in borax, forming beads, which, up to a certain stage of saturation, are clear. When these beads are brought into the reducing flame, and an intermittent blast is used, they become opaque. This is what is known as *flaming*. Tin, lead, and silver are used to facilitate the reduction of CuO , Fe_2O_3 , TiO_2 , and WO_3 . The beads, charged with the substance to be tested, are formed on the Pt wire, and while hot shaken off into a porcelain plate, and when a sufficient number is obtained, they are fused on charcoal into a large bead, and the metal added.

DIRECTIONS FOR FILMS—The *metallic* incrustations are obtained by heating a small particle of the substance on an asbestos fiber in the *reducing* flame of a Bunsen burner, under a glazed porcelain capsule half filled with water to keep it cool. On touching the *metallic* incrustations with a drop of dilute (20 per cent. of N_2O_5) HNO_3 on a glass rod:

<i>instantly dissolve,</i>	<i>slowly and difficultly dissolve,</i>	<i>unaffected,</i>
<hr/>	<hr/>	<hr/>
Pb, Cd, Zn, In.	Bi, Hg, Th.	Te, Se, As, Sb.

The substance to be tested is held in the upper oxidizing flame to form an *oxide* incrustation. When an asbestos fiber, wrapped with Pt, is soaked in a saturated solution of iodine in alcohol, and burned under the *oxide* incrustation, it forms the *iodide* incrustation; the solubility of the *iodide* incrustation is tested by the moist breath. When $(\text{NH}_4)_2\text{S}$ is blown upon the iodide or oxide incrustation, it forms the *sulphide* incrustation. The oxide incrustation is also rubbed with a glass rod dipped in AgNO_3 , and NH_3 vapor blown upon it.

118. Minerals are also tested by the *fusibility* of small splinters held in the platinum forceps in the fusing cone.

In using the blowpipe, it is important to remember that a trial of fusibility with the forceps, if not at once producing fusion, should be made on a piece of the mineral not larger than an ordinary pin-head, and it should be either oblong and slender, or thin, and be made to project considerably beyond the points of the forceps, lest the forceps carry off the heat.

Von Kobell has arranged a scale by which the fusibility of the substance may be compared with that of certain minerals of known fusibility.

1. *Stibnite*, fusible in the flame of a candle, in splinters.
2. *Natrolite*, fusible in the flame of a candle in fine splinters, easily fusible before the blowpipe.
3. *Almandine*, infusible in the candle flame, but fusible before the blowpipe.
4. *Actinolite*, fusibility less than almandine, and greater than orthoclase.
5. *Orthoclase*, fusible in fine splinters before the blowpipe.
6. *Bronzite*, fusible on the edges in very fine splinters.

The various gradations of fusibility are expressed by decimals; thus, 3.8 denotes a mineral which is less fusible than almandine and more than actinolite.

119. Minerals are also tested by the *scale of hardness*—Mohs's scale, with substitutes:

1. *Talc*, yields easily to the nail; as, embolite, molybdenite.
2. *Gypsum*, yields with difficulty to the nail, and does not scratch a copper coin; as, graphite, lead.
- 2.5. *Foliated mica*; as, cryolite, halite, galenite.
3. *Spar* (calcareous), scratches a copper coin, or about the same hardness; as, bornite, serpentine.
4. *Fluor spar*, does not scratch glass, and is not scratched by a copper coin; as, fluorite, siderite.
5. *Apatite*, scratches glass with difficulty, and yields readily to the knife; as, calamine, franklinite.

5.5. *Scapolite*, crystalline variety; as, chromite, cobaltite, lapis lazuli.

6. *Orthoclase*, scratches glass easily, and yields with difficulty to the knife; as, labradorite, oligoclase, turquoise.

7. *Quartz*, yields to the file, but not to the knife; as, boracite, garnet, spodumene.

8. *Topaz*, does not yield to the file; as, spinel.

9. *Sapphire* or corundum.

10. *Diamond*.

120. Minerals are also tested by the *streak*. The streak of a mineral is made by scratching it with a knife or file, or by drawing it across a piece of unglazed porcelain, and the color of the mark which it leaves behind is observed. The following are a few examples:

1. *Metallic streak*—tetradymite, bismuthinite, stibnite.

2. *Non-metallic streak*—cobaltite, grayish black; manganese, reddish brown; pyrolusite, black; franklinite, reddish brown; limonite, brownish yellow.

3. *Streak nearly the same as their color*—orpiment, lemon yellow; realgar, bright red; arseolite, white; valentinite, white; cinnabar, red; minium, red; salmiac, white; hematite, red.

121. Minerals are also tested by their *specific gravity*. Ordinary rock has a specific gravity of about 2.5. The ores of the heavy metals have a high specific gravity. Mountain leather and mountain cork, varieties of asbestos, float upon water. Iridosmine has a specific gravity of from 19 to 21.

122. Minerals are also tested by their *lustre*. Metallic, the lustre of metals; vitreous, lustre of broken glass, as quartz and calcareous spar; resinous, the lustre of yellow resin, as opal, zinc blende; pearly, as talc, magnesite, stilbite; silky, as calcite, gypsum; adamantine, the lustre of diamonds, as white lead ore or cerussite.

123. Minerals are also tested by their *color*, either metallic or unmetallic. The metallic are named after some familiar metal, as copper red, gold yellow, steel gray, etc. The unmetallic are various shades of white, gray, blue, green, yellow, red, and brown; play of colors, as the diamond and precious opal; change of colors, as the labradorite; opalescence, as in opals and in cat's eye; iridescence, as in quartz.

124. Minerals are also tested by their *taste, odor, and feel*. *Taste* belongs to soluble minerals—astrigent, as ZnSO_4 ; sweetish astrigent, as alum; saline, as NaCl ; alkaline, as soda; cooling, as KNO_3 ; bitter, as MgSO_4 ; sour, as KHSO_4 . *Odor*, the odor is given by friction, moistened with the breath, the action of acids, and the blowpipe—alliacious, the odor of garlic, as by burning As; horse radish odor, by burning selenium; sulphurous, by burning sulphur or pyrites; fetid, the odor of rotten eggs or H_2S (it is elicited by friction from some varieties of quartz and limestone); argillaceous, the odor of moistened clay, as serpentine and allied minerals when breathed upon, pyrargillite affording it when heated. Some minerals have a greasy feel, as the steatites and graphite. In some cases, refraction, polarization, electricity, magnetism, inflammability, and crystalline form give important information. Any one of these tests is insufficient for all of the elements but each is good for several of them. Negative tests are not given, and the student should for himself select those tests which he finds most serviceable under his handling. He should also make out a table, giving his results, in a systematic form.

NOTICE—Borax beads (116) are especially valuable for Mn, Co, Cu, Cr, Fe, Fe + Ti, and U; phosphorus beads for SiO_2 ; the film tests (117) for Bi, Hg, As, Sb, and Cd; the nascent H (114), for Cr and Mo, by deposits for As (octahedral crystals), and by gas for H_2S , H_3As , and H_3P ; the color tests (110) are good for Na, K, Cs, Ru, Ba, Sr, Li, Ca, Cu, B (As, Sb, Pb); the tests of fusibility, hardness, streak, specific gravity, lustre, color, odor, etc., for special mineralogy.

125. Prof. Egleston's Scheme of Blowpipe Analysis.

The substance may contain As, Sb, S, Se, Fe, Mn, Cu, Co, Ni, Pb, Bi, Ag, Au, Hg, Zn, Cd, Sn, Cl, Br, I, CO_2 , SiO_2 , N_2O_5 , H_2O .

1. Treat on charcoal in the O. F. to find volatile substances, such as As, Sb, S, Se, Pb, Bi, Cd, etc.

a. If there are volatile substances present, form a coating and test it with phosphorus salt and tin on charcoal for Sb (110) or to distinguish between Pb and Bi (110).

b. If there are no volatile substances present, divide a part of the substance into three portions, and proceed as in 1.

(*a*) Yellow coat, yielding with phosphorus salt a black bead; disappearing with blue flame; no part of it yielding greenish Sb flame; Pb and Bi.

(*b*) Yellow coat, generally with white border, yielding black or gray bead with phosphorus salt, disappearing with blue flame; also the border, disappearing with greenish flame; Pb and Sb.

(*c*) Yellow coat, very similar to (*b*), but yielding no blue flame; Bi and Sb.

2. If As, Sb, S, and Se are present, roast a large quantity thoroughly on charcoal until no odor of arsenic or sulphurous acid is given off. Divide the substance into three portions, and proceed as in 1.

1. *Treatment of the First Portion*—Dissolve a very small quantity in borax on Pt wire in the O. F., and observe the color produced. Various colors will be formed by the combination of the oxides. Saturate the bead, and shake it off into a porcelain dish. Repeat this once or twice.

(*a*) Treat these beads on charcoal with a small piece of lead, silver, or gold in a strong R. F.

(*b*) Fe, Mn, Co, etc., remain in the bead. If the bead spreads out on the charcoal, it must be collected to a globule by continued blowing. Make a borax bead on Pt wire, and dissolve in it *some* of the fragments of the bead, reserving the rest for accidents.

(*c*) Ni, Cu, Ag, Au, Sn, Pb, and Bi are reduced and collected by the lead button (Sn, Pb, Bi, if present, partly volatilize). Remove the lead button from the bead while hot, or by breaking the latter when cold, on the anvil between paper, carefully preserving all the fragments.

(*d*) If Co is present, the bead will be blue. If a large amount of Fe is present, add a little borax to prove the presence or absence of Co. If Mn is present, the bead, when treated on Pt wire in the O. F., will become dark violet or black.

(e) If only Fe and Mn, with no Co, are present, the bead will be almost colorless. Look here for Cr, Ti, Mo, U, W, V, Ta, by the wet way.

(f) Treat the button (c) on charcoal in the O. F. until the lead, etc., is driven off, Ni, Cu, Ag, and Au remaining behind; or separate the lead with boracic acid.

(g) Treat the residue (g) on charcoal in the O. F. with phosphorus salt bead, removing the button while the bead is hot.

(h) If Ni and Cu are present, the bead will be green when cold. If Ni only, yellow; if Cu only, blue. Prove Cu by treating with tin on charcoal in the R. F.

(i) For Ag and Au, make the special test.

2. *Treatment of the Second Portion*—Drive off all the volatile substances in the O. F. on charcoal. Treat with the R. F., or mix with soda, and then treat with the R. F. for Zn, Cd, and Sn. If a white coating is formed, test with cobalt solution (110).

3. *Treatment of the Third Portion*—Dissolve some of the substance in phosphorus salt on Pt wire in the O. F., observing whether SiO_2 is present or not, and test for Mn with potassium nitrate.

3. Test for As with soda on charcoal in the R. F., or with *dry* soda in closed tube (110).

4. Dissolve in soda on Pt wire in the O. F. (if the substance is not metallic and does not contain any S), and test for Sb on charcoal, with tin in the R. F. (110).

5. Test for Se on charcoal (110).

6. In absence of Se, fuse with soda in the R. F., and test for S on silver foil (111). In presence of Se, test for S in open tube (111) to distinguish between S and SO_3 .

7. Test for Hg with *dry* $\text{Na}_2\text{CO}_3 + \text{C}$ in a closed tube (107).

8. Mix some of the substance with assay lead and borax glass, and fuse on charcoal in the R. F. Cupel the lead button for Ag. Test with nitric acid for Au (113).

9. Test for Cl, Br, and I with a bead of phosphorus salt, saturated with oxide of copper (110). With Br the flame is blue, with green tint; with I, the flame is green.

10. Test for Cl or Br with acid sulphate of potassium.

11. Test for H_2O in a closed tube (106).

12. Test on Pt wire or in Pt pointed forceps, for coloration in the flame (110).

13. Test for CO_2 with HCl (106).

14. Test for N_2O_5 with acid sulphate of potassium.

15. Test for Te in an open tube (108).

CHAPTER III.

TESTS IN THE WET WAY.

126. The first duty of the student will be to get the substance into a state of solution, before he can make any tests.

Organic matter, as sugar, tartaric and citric acids, prevents the formation of some precipitates; as, $\text{Fe}(\text{OH})_2$, and renders others uncertain. While testing for bases, their presence should be first determined, and these matters destroyed, if necessary. Roast a small portion of the substance in a small tube or on Pt foil; carbon is indicated if the substance chars. Heat on Pt foil after making an intimate mixture with KNO_3 ; if it deflagrates, carbon is present. If carbon is indicated, roast a portion on Pt foil in free air; if it burns to a white mass, it indicates carbon. Remove organic matters by ignition in free air, when no volatile bodies, as As or Hg, are present; if volatile bodies are present, treat all with $\text{HCl} + \text{KClO}_3$.

Decompose compound cyanides by heating with strong H_2SO_4 in a good draught of air, and expel most of the H_2SO_4 by prolonged heating.

127. When no organic matters are present, make a careful preliminary examination of the substance, to obtain some clue to the kind of solvent required. Test a small portion of the substance with each of the liquid solvents named below, until a complete solution is obtained. Determine in each case if a partial solution is obtained, by filtering the liquids and evaporating a portion on Pt foil.

128. A substance having a metallic lustre may be a metal, an alloy, or an ore containing S, As, or Sb. Reduce to a fine powder.

Boil with strong HNO_3 . It oxidizes most metals, and dissolves them as nitrates; oxidizes S to H_2SO_4 , As to As_2O_5 . If a *white residue is left*, it may be $\text{Pb}(\text{NO}_3)_2$, PbSO_4 , SnO_2 , Sb_2O_3 , etc.; filter and wash.

Treat this residue with H_2O , and boil; $\text{Pb}(\text{NO}_3)_2$ dissolves. Add this to the portion already dissolved. Add a strong solution of $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, and boil; Sb_2O_3 dissolves. Test by H_2S . Add NH_4HO to the $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ solution, and again boil; PbSO_4 dissolves. Test by H_2S . SnO_2 remains. Reduce on charcoal by $\text{KCN} + \text{Na}_2\text{CO}_3$. Dissolve the metallic bead in HCl , and test for SnCl_2 ; or treat this white residue with NH_4HS ; SnO_2 , Sb_2O_3 dissolve; Pb becomes black PbS . If, on adding $\text{H}_2\text{O} + \text{NH}_4\text{Cl}$ to the solution in HNO_3 , a white cloudiness appears, Bi may be present.

If a colored residue is left, it may be gold, the platinum metals, or carbon, silicon, or sulphur. Pt and Au dissolve in aqua regia. The S ignites when heated on Pt foil, and yields SO_2 . The carbon may have come from the process of smelting, as in cast iron. It burns away before the blowpipe on Pt foil. The silicon leaves, on ignition before the blowpipe, a white residue. Test by microcosmic salt.

129. Substances which have no metallic lustre. Reduce to a very fine powder. Boil a small portion with H_2O . If all dissolves, or the greater part, treat the entire quantity with H_2O , and filter.

Treat a small portion of the residue insoluble in H_2O , with dilute HCl . Add H_2O , and boil. If much dissolves, treat all with HCl . Gases like H_2S , SO_2 , CO_2 may be given off. Sb and Bi solutions become turbid when H_2O is added.

Treat a small portion of the residue insoluble in H_2O and in HCl , with HNO_3 . Treat this last residue with concentrated HCl . Peroxides like MnO_2 , PbO_2 evolve Cl . Treat this last residue

with aqua regia, or with $\text{HCl} + \text{KClO}_3$. The solutions which may have been obtained by these various processes may be examined separately, as is sometimes necessary in testing for acids; or, if Pb, Ag, Hg, are absent, they may be mixed together in testing for bases.

In this treatment with acids, SiO_2 may have dissolved. If this is suspected, evaporate the solution to complete dryness, moisten with HCl, and again dry thoroughly. The SiO_2 thereby becomes insoluble.

By these methods we cannot expect to dissolve AgCl, metallic fluorides, sulphates of Pb, Ba, Sr, most silicates, and SiO_2 , many strongly ignited oxides, as those of Fe, Cr, Sn, Al, Sb, Ti, W, Nb, Ta, nor all the free S, nor carbon. If AgCl is present in this residue, it may be dissolved out by $(\text{NH}_4)\text{HO}$. The others require special treatment, as follows:—

130. Substances which are insoluble in H_2O , in HCl, in HNO_3 , and in aqua regia. Examine this insoluble residue by the preliminary tests. (Chapter II.)

Test for C and S by Heating on Pt Foil in the Oxidizing Flame—If these are present, oxidize thoroughly. After oxidizing the substance, test by microcosmic salt. It will indicate SiO_2 , Cr, Fe, Ti, W, Ta, Nb; test for the last four by $\text{Zn} + \text{HCl}$. Heat a portion on charcoal with $\text{Na}_2\text{CO}_3 + \text{KCN}$. It will give hepar with Ba, Sr, Ca, Pb sulphates; reduces metals like Sn, Fe, Pb, Sb, Ag. Test for Al on charcoal and with $\text{Co}(\text{NO}_3)_2$. Test for F by treatment with strong H_2SO_4 ; the HF evolved etches glass. The further treatment of these insoluble bodies depends upon the indications which are then obtained.

131. If the *very finely* pulverized substance is mixed with four times its weight of Na_2CO_3 , or better, NaKCO_3 , and thoroughly fused, (a) BaSO_4 , SrSO_4 , CaSO_4 , PbSO_4 become Pb, BaCO_3 , SrCO_3 , CaCO_3 . The SO_4 unites with the Na to form Na_2SO_4 ; (b) silicates, fluorides, titanates, etc., chromates, aluminates, stannates, antimonates, give soda salts, soluble in H_2O .

If the *very finely* pulverized substance is mixed with eight times its weight of KHSO_4 and thoroughly fused, (a) ignited oxides like Fe_2O_3 , Al_2O_3 , Cr_2O_3 , either form salts soluble in H_2O , or leave a residue soluble in HCl or HNO_3 . (b) This is the best method for titanates, etc.

Most of these substances if mixed, when finely pulverized, with two parts of charcoal and twelve parts of KNO_3 in a porcelain dish and ignited, yield a mass which is partly soluble in H_2O , and the residue in HCl .

It is often advisable to treat filings of alloys and substances which contain As, Sb, Sn with NH_4HS . This dissolves out the As, Sb, Sn, and leaves most of the metals as sulphides, which are soluble in HNO_3 .

132. When a Solution has been made by any one of these methods, it must be remembered that any excess of an acid must be expelled by evaporation before applying tests for bases; and that any excess of alkali must be neutralized before applying tests for acids.

Often when only a single substance, known to be present, is to be determined, special modes of separation may be applied at once.

- (a) Fluorides are decomposed by H_2SO_4 .
- (b) Silicates are decomposed by HF .
- (c) The platinum metals, As, etc., are converted to chlorides by chlorine gas.
- (d) Most of the metallic sulphides and oxides when heated are reduced by H gas, or by nascent hydrogen; *i. e.*, $\text{Zn} + \text{HCl}$.

133. In qualitative chemical analysis, the metals or bases are commonly divided into five groups.

GROUP I.—SILVER GROUP.

This comprises those metals whose chlorides are practically insoluble in water, and which are, therefore, precipitated by the group reagent, hydrochloric acid. These are *silver*, *lead*, and

mercury (monad mercury or mercurosum), and the *rare elements*, tungsten, thallium, and niobium. This is called the *silver group*.

When Ag is absent, Pb and Hg are easily detected along with the elements of the next group.

134. Silver (Ag^I , 108*). The solution of the nitrate is the one used for testing.

The best solvent for silver is HNO_3 . Hot concentrated H_2SO_4 forms sulphate, which is sparingly soluble. Fixed alkalis do not act upon Ag in the wet or dry way. The nitrate, acetate, and sulphate form *anhydrous* crystals. The orthophosphate and arsenite are yellow; the arseniate, reddish-brown; the iodide, yellow; the bromide, yellowish-white; the sulphide, black. The salts of silver are chiefly *colorless*, and the normal salts are neutral to litmus. The oxide, sulphide, chloride, bromide, bromate, iodide, iodate, cyanide, ferrocyanide, ferricyanide, carbonate, oxalate, phosphate, arsenite, arseniate, sulphite, and tartrate are *insoluble* in H_2O , or sparingly soluble.

The fixed alkaline hydroxides precipitate, in the absence of organic acids, *silver oxide*, Ag_2O , grayish-brown, insoluble in excess of reagent. By reduction of silver salts, an argentous oxide, Ag_4O , and a corresponding chloride may be formed. By the action of ozone on the metal, Ag_2O_2 is formed.

Silver combines with Cl, Br, and I at ordinary temperatures, and readily with S, P, and As on heating.

135. Tests:—

1. Easily reduced to metallic Ag before the blowpipe, on charcoal.

2. HCl precipitates *white* AgCl , insoluble in HNO_3 , soluble in NH_4HO .

3. H_2S or $(\text{NH}_4)_2\text{S}$ precipitates *black* Ag_2S , insoluble in dilute acids, in alkalies, alkaline sulphides, potassium cyanide; soluble in boiling HNO_3 .

* The atomic weights are whole numbers.

4. NaHO , KHO , and NH_4HO precipitate *light-brown* Ag_2O , insoluble in excess of NaHO or KHO , but soluble in excess of NH_4HO . If the solution is acid NH_4HO does not precipitate AgNO_3 .

5. Na_2CO_3 precipitates *grayish-white* Ag_2CO_3 , soluble in NH_4HO .

6. Na_2HPO_4 precipitates *yellow* Ag_3PO_4 , soluble in HNO_3 , H_3PO_4 , and in NH_4HO .

7. KI precipitates *yellow* AgI , insoluble in NH_4HO , soluble in excess of reagent.

8. KBr precipitates *white* AgBr , slightly soluble in excess.

9. $\text{K}_2\text{Cr}_2\text{O}_7$ precipitates *dark-red* Ag_2CrO_4 , soluble in HNO_3 and in NH_4HO ; decomposed by HCl into white AgCl .

10. Zn , Cu , Fe , Mg , Pb , Bi , Hg , reduce silver solutions to the metallic state, best from its solution as cyanide (*arbor Dianæ*).

11. $\text{K}_4\text{FeC}_6\text{N}_6$ precipitates *white* $\text{Ag}_4\text{FeC}_6\text{N}_6$, difficultly soluble in NH_4HO .

12. $\text{Na}_2\text{S}_2\text{O}_3$ precipitates *white* $\text{Ag}_2\text{S}_2\text{O}_3$, soluble in excess.

Light decomposes most compounds of Ag , with blackening from formation of metallic Ag , or of Ag_4O , or of both.

The nitrate and chloride fuse undecomposed, but are decomposed at higher temperatures. The nitrate, phosphate, iodide, and cyanide are not decomposed by light alone.

Almost all the salts of silver are freely soluble in ammonia. AgCl is easily soluble, AgBr is difficultly soluble, and AgI is almost insoluble.

136. Lead ($\text{Pb}^{\text{II-IV}}$, 207). It is generally obtained from galena, PbS . It is a soft metal, of bluish lustre, which is easily tarnished. When heated in the air, it oxidizes, first to litharge, PbO , and then to minium, or red lead, Pb_3O_4 . When either of these oxides is treated with HNO_3 , $\text{Pb}(\text{NO}_3)_2$ is formed; but when the higher oxide is used, there remains behind a brown powder, PbO_2 , known as puce colored oxide of lead. It is possible that red lead is a mixture of 2PbO , PbO_2 . Only the protoxide enters into combination with acids, and its salts are generally

insoluble in water. Notably the sulphate, oxalate, carbonate, chromate, sulphite, phosphate, oxide, hydroxide, chloride, iodide, bromide, and ferrocyanide are sparingly soluble in water. The nitrate and acetate are soluble in water, either of which can be employed in the tests. Lead combines directly with S, P, As, and most of the metals. The lead salts are non-volatile; most of them are colorless. The normal salts redden litmus paper, and are decomposed at a red heat.

137. Tests:—

1. From solutions of lead acetate or nitrate, the fixed alkalis precipitate *white* $\text{Pb}(\text{OH})_2$, soluble in excess of the reagent, by combination, as potassium plumbite, K_2PbO_2 .

2. Heated before the blowpipe, on charcoal, with dry Na_2CO_3 , give metallic Pb, and a yellow coating or incrustation of PbO.

3. Metallic Zn precipitates Pb in crystals (*arbor Saturni*).

4. H_2S or $(\text{NH}_4)_2\text{S}$ precipitate *black* PbS , insoluble in excess; soluble in HNO_3 , and converted into PbSO_4 (detects one part in 100,000).

5. H_2SO_4 precipitates *white* PbSO_4 , insoluble in alcohol, soluble in strong H_2SO_4 . PbSO_4 is soluble in 1,300 parts of water; more readily soluble in some ammoniacal salts.

6. $(\text{NH}_4)_2\text{CO}_3$ precipitates *white* PbCO_3 . See No. 7.

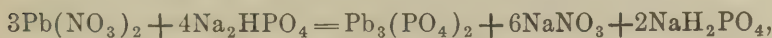
7. Na_2CO_3 precipitates basic lead carbonate, $\text{PbCO}_3 + \text{Pb}(\text{OH})_2$, in various proportions, according to temperature and concentration.

8. HCl precipitates *white* PbCl_2 , soluble in 30 parts of water, insoluble in alcohol, and ammonium hydroxide.

9. $\text{K}_2\text{Cr}_2\text{O}_7$ precipitates *yellow* PbCrO_4 , insoluble in dilute HNO_3 , and insoluble in NH_4HO ; soluble in fixed alkalis.

10. KI precipitates *yellow* PbI_2 , soluble in large excess on heating. (Soluble in 1,900 parts of cold and 200 parts of hot water.)

11. Na_2HPO_4 precipitates *white* $\text{Pb}_3(\text{PO}_4)_2$, insoluble in dilute acetic acid, soluble in HNO_3 and fixed alkalies.:



if there is an excess of phosphate.

138. Mercury ($\text{Hg}^{\text{I-II}}$, 200). It is liquid at temperatures between -40°C . and 360°C . It is slightly volatile at ordinary temperatures. It enters into combination with Cl and Br at ordinary temperatures. It combines with I and S in the cold, if triturated with them. It combines with most of the metals at ordinary temperatures, forming alloys, which are called amalgams. At ordinary temperatures it is but little acted upon by HCl; strong H_2SO_4 , when heated, dissolves it with moderate rapidity, evolving SO_2 . HNO_3 is the best solvent. It forms two oxides, Hg_2O black and HgO red or yellow, and two corresponding classes of salts, mercurous and mercuric compounds. Their solutions redden litmus. The chlorides: mercurous chloride, Hg_2Cl_2 , is insoluble in water; the mercuric chloride, HgCl_2 , is soluble in water.

The reactions in the dry way are nearly the same for both *ous* and *ic* compounds. Only the *mercurous* compounds will be described here, the mercuric at No. 143. The mercurous salts volatilize upon ignition, and most of them are decomposed by this process; the Hg_2Cl_2 and Hg_2Br_2 volatilize unaltered. The salts are generally colorless. Most of the *ous* compounds (except the normal nitrate) are insoluble in water.

139. Tests:—

1. All compounds of mercury, when dry and heated with dry Na_2CO_3 in a tube closed at one end, give a sublimate of metallic mercury.

2. Copper foil precipitates silvery spots of metallic mercury.

3. NaHO or KHO precipitates *black* Hg_2O , insoluble in alkalies, soluble in HNO_3 .

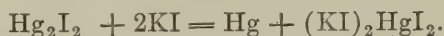
4. NH_4HO precipitates *black* $(\text{NH}_2\text{Hg}_2)\text{NO}_3$, insoluble in alkalies, soluble in acids.

5. H_2S or $(\text{NH}_4)_2\text{S}$ precipitates *black* Hg_2S with HgS and Hg , insoluble in HNO_3 , HCl , $(\text{NH}_4)_2\text{S}$; sparingly soluble in K_2S Na_2S .

6. HCl precipitates *white* Hg_2Cl_2 , calomel, soluble in NH_4Cl , in aqua regia, in HNO_3 , blackens by NH_4HO .



7. KI precipitates *greenish yellow* Hg_2I_2 , insoluble in H_2O and in $\text{C}_2\text{H}_6\text{O}$. By excess becomes



8. $\text{K}_2\text{Cr}_2\text{O}_7$ precipitates *orange* Hg_2CrO_4 or a basic chromate, soluble in HNO_3 .

9. $\text{K}_4\text{FeC}_6\text{N}_6$ precipitates *white gelatinous* $\text{Hg}_4\text{FeC}_6\text{N}_6$; $\text{K}_3\text{FeC}_6\text{N}_6$, a red brown precipitate.

10. Na_2CO_3 precipitates *gray* Hg_2CO_3 , blackening to a basic carbonate and oxide when heated.

11. Soluble sulphates precipitate *white* Hg_2SO_4 , soluble in 500 parts H_2O .

140. Separation of the Silver Group.

HCl added to $\text{AgNO}_3 + \text{Pb}(\text{NO}_3)_2 + \text{Hg}_2(\text{NO}_3)_2$ precipitates *white* $\text{AgCl} + \text{PbCl}_2 + \text{Hg}_2\text{Cl}_2$, filter and boil the precipitate with water.

SOLUTION.	RESIDUE.	
PbCl_2 , on cooling, acicular crystals. Add H_2SO_4 , precipitates <i>white</i> PbSO_4 . Reduce with carbon and Na_2CO_3 to metallic Pb ; dissolve in dilute HNO_3 , and add $\text{K}_2\text{Cr}_2\text{O}_7$, <i>yellow</i> PbCrO_4 .	AgCl .	Hg_2Cl_2 .
	Add NH_4HO .	
	SOLUTION.	RESIDUE.
	AgCl , add HNO_3 .	$\text{NH}_2\text{Hg}_2\text{Cl}$, <i>black</i> .
	AgCl . Reduce on charcoal to metallic Ag ; dissolve in dilute HNO_3 , add $\text{K}_2\text{Cr}_2\text{O}_7$, <i>red</i> Ag_2CrO_4 .	Reduce in a glass tube with carbon and Na_2CO_3 , sublimate of Hg . Dissolve in HNO_3 and confirm with KI , <i>red</i> HgI_2 . See No. 139.

141. Notes on the first group.

1. The separation of the first group is quite simple. The PbCl_2 is dissolved in an abundance of *hot water*; AgCl in *ammonium hydroxide*; while Hg_2Cl_2 is left undissolved as a *black* $\text{NH}_2\text{Hg}_2\text{Cl}$.

2. When only one member of the group is present as a precipitate, NH_4HO determines which it is; PbCl_2 does not change color; AgCl dissolves; Hg_2Cl_2 blackens.

3. The group reagent, HCl , *completely* precipitates Ag and Hg , and *partially* precipitates Pb , as the PbCl_2 is soluble in 135 parts of cold water and 30 parts of *hot water*.

4. *In all mixtures of the bases* that the student does not make for himself, the condition of the solution (acid, neutral, or alkaline) must be determined before the group reagent is added.

THE GROUP REAGENT HCl .

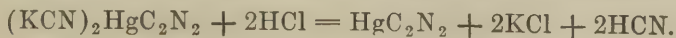
5. HCl may precipitate *sulphur* from alkaline solutions containing Na_2S or $\text{Na}_2\text{S}_2\text{O}_3$.

6. Saturated solutions of chlorides, as BaCl_2 , are precipitated unchanged as BaCl_2 .

7. Solutions of Bi , Sb , and Sn may be precipitated as the *oxychloride* of the metal in question.

8. Certain volatile acids may be expelled; as CO_2 , H_2S , and HCN .

9. Certain double salts, as sulphides, cyanides, iodides, thiosulphates, may be broken up and precipitates formed:



10. Alkaline solutions of metallic oxides, as K_2O , ZnO , may be precipitated when neutralized by acids.

11. HCl may precipitate certain alkaline solutions of boracic, silicic, antimonie (tungstic, molybdic, tantalic, and

niobic), acids, and certain organic acids, as benzoic, salicylic, and uric.

N. B.—In using a reagent, use enough to precipitate the substance sought *completely*, and test the filtrate to ascertain if this has been done; but care should be taken not to add too much—a drop too much is excess.

GROUP II.—LEAD AND ARSENIC GROUP.

142. The second group comprises those metals that are precipitated from their *slightly acid* solutions, as *sulphides*, by the group reagent H_2S . They are Ag, Hg, Pb, Bi, Cu, Cd, and As, Sb, Sn; the *rare elements*, palladium, rhodium, osmium, ruthenium, platinum, iridium, gold, molybdenum, selenium, tellurium, and tungsten.

143. Mercury (Hg^{II} , 200). As *mercuric* compounds. The oxide, basic carbonate, tartrate, sulphide, ferrocyanide, iodide, iodate, arsenite, arseniate, phosphate, and oxalate are *insoluble* in water. The chromate and citrate are sparingly soluble. The *ous* salts of mercury are easily changed by oxydizing agents to the *ic* salts. The ordinary mercuric salts (except the chloride) which are soluble in water, seem to require the presence of *free* acid, being partially decomposed by water, with the separation of *basic* salts. The reactions are modified by the free acid, as in the case of mercuric nitrate.

144. Tests:—

1. In the *dry way*, the same as the *ous* compounds.
2. $Cu(Zn, Fe)$ precipitates metallic Hg.
3. H_2S or $(NH_4)_2S$ precipitates *white* $HgSHgCl_2$; on the addition of an excess of the reagent, it is converted into *black* HgS , insoluble in HNO_3 or HCl , soluble in *aqua regia* and in *alkali hydroxides*; it is also soluble in *free* chlorine.
 - (a) $HgS + Cl_2 = HgCl_2 + S$.
 - (b) $HgS + K_2S = K_2S, HgS$.
 - (c) $2HgS + 2KHO = K_2S, HgS + HgO + H_2O$.

The black sulphide, when heated and rubbed, is converted into red (vermilion) without chemical change.

4. Reducing agents (SnCl_2 , SO_2 , $\text{Na}_2\text{S}_2\text{O}_3$) first *white* Hg_2Cl_2 , then *gray* Hg .

5. Fixed alkali hydroxides (NaHO , KHO) precipitate *red-dish-brown basic salts*; with excess of reagent, HgO , insoluble in alcohol and in ammonium hydroxide, soluble in 200,000 parts of water.

6. NH_4HO precipitates *white* $(\text{NH}_2\text{Hg})\text{Cl}$, soluble in HCl , sparingly soluble in NH_4HO .

7. Na_2CO_3 or K_2CO_3 precipitates *reddish-brown* basic salt, 3HgO , HgCO_3 , converted into the yellow oxide HgO .

8. Soluble *iodides* (KI) precipitate *red* HgI_2 , soluble in an excess of either reagent.

9. K_2CrO_4 precipitates *yellowish-red* HgCrO_4 , soluble in HNO_3 , sparingly soluble in water.

10. Soluble *phosphates* (Na_2HPO_4) precipitate *white* $\text{Hg}_3(\text{PO}_4)_2$, soluble in acids and in NH_4HO salts.

145. Lead ($\text{Pb}^{\text{II-IV}}$, 207). See No. 136.

146. Bismuth (Bi^{III} , 210). Bismuth melts at 264°C . It readily combines with Cl , Br , I , and S . Nitric acid is the best solvent. Bismuth forms one stable oxide, Bi_2O_3 , *yellowish white*; the oxide, Bi_2O_2 , is *black*; Bi_2O_5 is *red*. The oxides and hydroxide, $\text{Bi}(\text{OH})_3$, are readily soluble in dilute mineral acids.

The bismuth salts are white, non-volatile, and are decomposed at a red heat (the trichloride is volatile). The chloride is deliquescent; the nitrate, permanent. All the salts have a tendency to *basic formations*, and many are decomposed by a large quantity of water into *insoluble basic* and *soluble acid* salts.

The most of the normal salts are soluble in water acidulated with their respective acids, or with acids forming *soluble* bismuth salts; the decomposition of the normal sulphate, nitrate, and chloride is prevented by the addition of organic acids, as citric acid.

The sulphide, chromate, borate, sulphite, hydroxide, oxalate, iodide, basic carbonate, phosphate, tartrate, citrate, cyanide, ferrocyanide, ferricyanide, valerianate, and tannate are *insoluble* in water.

147. Tests:—

1. Fused with Na_2CO_3 , gives brittle bead, Bi, and yellow oxide, Bi_2O_3 , coating.

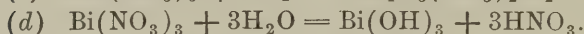
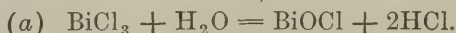
2. $\text{Bi} + \text{S} + \text{KI}$, heated on charcoal before the blowpipe, gives bright *scarlet-red* incrustation.

3. H_2S or $(\text{NH}_4)_2\text{S}$ precipitates *brownish-black* Bi_2S_3 , insoluble in KCN, $(\text{NH}_4)_2\text{S}$, and dilute acids; soluble in strong HNO_3 .

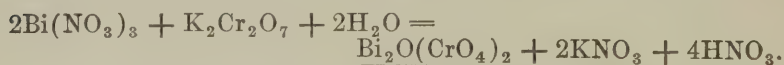
4. Alkali hydroxides (NaHO , KHO , NH_4HO) precipitate, in the absence of tartaric or other organic acids, *white* $\text{Bi}(\text{OH})_3$, insoluble in excess, soluble in HCl and HNO_3 .

5. Na_2CO_3 precipitates *white* $(\text{BiO})_2\text{CO}_3$, insoluble in excess, soluble in KCN; HCl and HNO_3 (best).

6. H_2O precipitates (best from the chloride) *white* BiOCl , insoluble in tartaric acid, soluble in HCl and HNO_3 .



7. $\text{K}_2\text{Cr}_2\text{O}_7$ precipitates *yellow* basic chromate, $\text{Bi}_2\text{O}(\text{CrO}_4)_2$, insoluble in NaHO , soluble in HNO_3 .



8. KI precipitates *brown* BiI_3 , soluble in excess of the reagent, in HCl and HI .

9. SnCl_2 , in the presence of NaHO or KHO , precipitates *black* Bi_2O_2 (very delicate reaction).

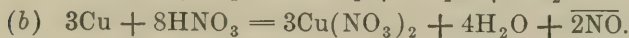
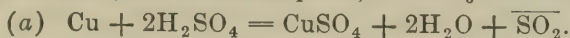
10. $\text{K}_4\text{FeC}_6\text{N}_6$ precipitates *white* $\text{Bi}_4(\text{FeC}_6\text{N}_6)_3$. The alkaline cyanides precipitates *white* $\text{Bi}(\text{OH})_3$ with the formation of HCN .

11. Oxalates ($\text{H}_2\text{C}_2\text{O}_4$) precipitate *white* $\text{Bi}_2(\text{C}_2\text{O}_4)_3$, insoluble in dilute acids.

12. Phosphates (Na_2HPO_4) precipitate *white* BiPO_4 , soluble in HCl and H_2SO_4 .

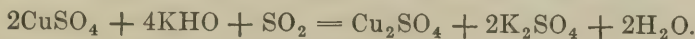
13. Bi is reduced from bismuthous solutions by Zn, Fe (Sn, Cu, Cd, Pb) as a spongy precipitate.

148. Copper ($\text{Cu}^{\text{I-II}}$, 63). When heated, it combines directly with Br, I, S, Si, etc. When it *dissolves* in an acid, H is not evolved (HI is an exception). HNO_3 is the best solvent.

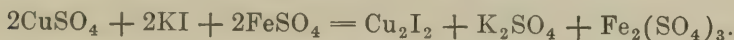


(c) CuCl_2 is formed when Cu is burned in an excess of Cl, or when the hydrated crystalline chloride is heated.

Copper forms two oxides: cuprous, Cu_2O , brownish red; cupric, CuO , black. The cuprous salts, Cu_2O , $\text{Cu}_2(\text{OH})_2$, Cu_2Cl_2 , are *insoluble* in water. The cupric are readily *reduced* to *cuprous* by strong reducing agents, acting *with alkalis*:



By ferrous salts in the presence of iodides:



Metallic Fe and Zn precipitate from cupric salts, metallic Cu without the formation of cuprous salts.

The following cupric salts are *insoluble* in water: Oxalate, borate, hydroxide, basic carbonate, tartrate, cyanide, sulphide, arsenite, ferro and ferri cyanides. The sulphate and acetate are insoluble in alcohol; the nitrate and chloride are soluble. The chloride is also soluble in ether.

149. Tests:—

1. Heated with Na_2CO_3 , upon charcoal, it is easily reduced to metallic Cu (red).

2. Fe and Zn precipitate from cupric solutions, Cu (Cu is also precipitated by Bi, Cd, Ni, Co, Sn, P):

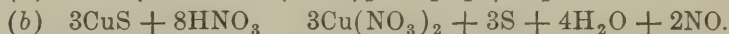
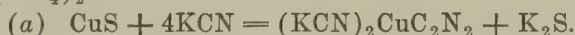


3. Fixed alkalis (KHO, NaHO) added to *saturation* precipitate *blue* $\text{Cu}(\text{OH})_2$, insoluble in excess; when boiled, becomes CuO : $\text{Cu}(\text{OH})_2 = \text{CuO} + \text{H}_2\text{O}$, or black, basic hydroxide $\text{Cu}_3\text{O}_2(\text{OH})_2$. Many *organic* substances, as tartaric acid, will prevent the formation of the precipitate, or redissolve it.

4. NH_4HO precipitates (short of saturation) *pale blue basic salts*, (saturation) *deep blue* $\text{Cu}(\text{OH})_2$; the precipitate dissolves to a *deep blue* solution (supersaturation):



5. H_2S or $(\text{NH}_4)_2\text{S}$ precipitates *brown-black* CuS , soluble in 950,000 parts of water, in KCN, in HNO_3 ; sparingly soluble in $(\text{NH}_4)_2\text{S}$.



6. Na_2CO_3 precipitates *greenish-blue* basic carbonate, $\text{CuCO}_3\text{Cu}(\text{OH})_2$; on boiling, it becomes CuO , and dissolves in NH_4HO and KCN to a colorless fluid.

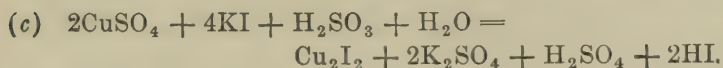
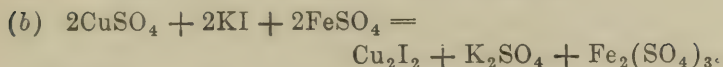
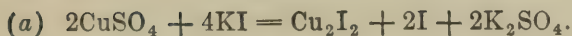
7. $\text{K}_4\text{FeC}_6\text{N}_6$ precipitates *red-brown* $\text{Cu}_2\text{FeC}_6\text{N}_6$, insoluble in dilute acids, but decomposed by KHO; slightly soluble in NH_4HO ; in dilute solutions, merely a reddish coloration.

8. $\text{K}_3\text{FeC}_6\text{N}_6$ precipitates *yellowish-green* $\text{Cu}_3(\text{FeC}_6\text{N}_6)_2$, insoluble in HCl.

9. Na_2HPO_4 precipitates *bluish-white* CuHPO_4 , if the reagent is in excess; $\text{Cu}_3(\text{PO}_4)_2$, if the copper salt is in excess. Slightly soluble in acetic acid.

10. Alkaline cyanides (KCN) precipitate *yellowish-green* CuC_2N_2 , soluble in excess and forming $(\text{KCN})_2\text{CuC}_2\text{N}_2$, which is unstable.

11. Soluble iodides (KI) precipitate, from concentrated solutions, *white* Cu_2I_2 . The liquid is dark brown from free iodine. When a reducing agent is added, the precipitate is free from iodine.



12. SnCl_2 precipitates *white* Cu_2Cl_2 only in concentrated solutions, soluble in HCl .

13. K_2CrO_4 precipitates *red-brown* CuCrO_4 , soluble in NH_4HO with green color.

14. Sugar, organic compounds, arsenious acid, with fixed alkali hydroxides, reduce cupric salts to cuprous oxide.

15. $\text{K}(\text{C}_2\text{H}_5)\text{COS}_2$ (potassium ethyl X anthate) precipitates *brownish* $\text{Cu}(\text{C}_2\text{H}_5\text{COS}_2)_2$; changes to a bright yellow. ($\text{KC}_2\text{H}_5\text{COS}_2$ is made by dissolving KHO in absolute alcohol, and adding bisulphide of carbon; filter, and dissolve the precipitate in water.)

16. *For detecting traces of Cu*—When the end of a Pt wire is inserted just within the eye of a large sewing needle, around which the wire is wound, and the coil left in a solution of Cu acidulated with acetic acid, at 30°C ., for a few hours, a black-brown stain or coating on the Pt wire indicates Cu. (Hager.)

150. Cadmium (Cd^{II} , 112). It has a tin-white color, melts at 350°C . HNO_3 is the best solvent. It forms a single oxide, CdO , *yellowish brown*; the hydroxide $\text{Cd}(\text{OH})_2$ is *white*. Both dissolve readily in HCl , H_2SO_4 , HNO_3 . The soluble normal salts redden litmus paper, and are decomposed at a red heat. Of the metals Ag, Hg, Pb, Bi, Cu, Cd, Cd is the only metal which can displace H in dilute H_2SO_4 .

The phosphate, oxalate, carbonate, sulphide, hydroxide, cyanide, ferrocyanide, and ferricyanide are *insoluble* in water. The chloride and bromide are *deliquescent*, and soluble in water and alcohol.

151. Tests:—

1. Heated on charcoal with Na_2CO_3 , it is reduced to Cd; it is easily oxidized to CdO with brown incrustation.

2. H_2S or $(\text{NH}_4)_2\text{S}$ precipitates *yellow* CdS, insoluble in dilute acids, alkalies, alkali sulphides, or cyanides. If the solution of Cd contains a large excess of acid, H_2S produces a precipitate only after dilution with water. The CdS is soluble in hot HCl , HNO_3 , and H_2SO_4 .

3. Mg precipitates from acid and ammoniacal solutions *gray* Cd; Zn also precipitates it.

4. Alkalies (NaHO , KHO) precipitate *white* $\text{Cd}(\text{OH})_2$, insoluble in excess; NH_4HO forms the same precipitate, soluble in excess. In the fixed alkalies, the presence of organic substances prevents the precipitation.

5. Na_2CO_3 or $(\text{NH}_4)_2\text{CO}_3$ precipitates *white* CdCO_3 , insoluble in excess; ammonium salts impede or prevent the precipitation.

6. KCN precipitates *white* $\text{Cd}(\text{CN})_2$, soluble in excess as $(\text{KCN})_2\text{Cd}(\text{CN})_2$; H_2S precipitates this solution as CdS.

7. KI precipitates *white* CdI_2 only in very concentrated solutions.

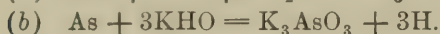
8. $\text{K}_4\text{FeC}_6\text{N}_6$ precipitates *yellowish-white* $\text{Cd}_2(\text{FeC}_6\text{N}_6)$; $\text{K}_3\text{FeC}_6\text{N}_6$ precipitates *yellow* $\text{Cd}_3(\text{FeC}_6\text{N}_6)_2$. Both precipitates are soluble in HCl and in NH_4HO .

9. Oxalates and oxalic acid precipitate *white* CdC_2O_4 , difficultly soluble in acids.

The chromates (alkali) form *yellow* CdCrO_4 only in concentrated solutions. Phosphates form *white* CdHPO_4 , readily soluble in acids.

152. Arsenic ($\text{As}^{\text{III-V}}$, 75.) It is a steel-gray, brittle, non-metallic element, volatilizing at 356°C ., the vapor having an alliaceous odor. It combines with Cl and Br in the cold, and

with I and S by the aid of heat. It is slowly attacked by the mineral acids; its proper solvent is aqua regia or Cl with water. Hot solutions of KHO or NaHO dissolve it.



As is slowly oxidized in *moist* air, at ordinary temperatures, to a black "sub-oxide" (fly powder), which is probably a mixture of As and AsO_3 . Arsenic forms two important *oxides*, As_2O_3 and As_2O_5 , arsenious and arsenic anhydrides.

153. Tests:—

As_2O_3 (CRYSTALLINE AND AMORPHOUS.)

Specific gravity, 3.738. Is a good reducing agent. Forms arsenites with the metals.

Forms arsenious acid,



which is easily converted into sulphides, As_2S_3 (orpiment),

with hydrogen, AsH_3 ;

with chlorine, AsCl_3 ;

with bromine, AsBr_3 ;

with iodine, AsI_3 .

1. H_2S precipitates *yellow* As_2S_3 ; best from HCl solution; soluble in alkalis and alkaline sulphides, insoluble in HCl.

2. AgNO_3 precipitates *yellow* Ag_3AsO_3 , soluble in dilute acids, NH_4HO , or NH_4HO salts.

3. CuSO_4 precipitates *yellowish-green* $\text{Cu}_3(\text{AsO}_3)_2$, soluble in NH_4HO , and in NH_4Cl .

As_2O_5 (AMORPHOUS.)

Specific gravity, 3.734. Is an active oxidizing agent. Forms arseniates with the metals.

Forms arsenic acid, H_3AsO_4 .

Forms sulphides, As_2S_5 (penta-sulphide).

1. H_2S precipitates *yellow* $\text{As}_2\text{S}_3 + \text{S}_2$; from acid solutions, appears slowly, hastened by boiling.

2. AgNO_3 precipitates *reddish-brown* Ag_3AsO_4 , soluble in acids, NH_4HO , or NH_4HO salts.

3. CuSO_4 precipitates *greenish-blue* CuHAsO_4 , soluble in NH_4HO , NH_4Cl .

4. $(\text{NH}_4)_2\text{S}$ precipitates As_2S_3 only in acid solutions, soluble in excess of $(\text{NH}_4)_2\text{S}$.

5. *Ferric salts and fresh ferric hydroxide precipitate basic ferric arsenites*, insoluble in $\text{HC}_2\text{H}_3\text{O}_2$, soluble in HCl .

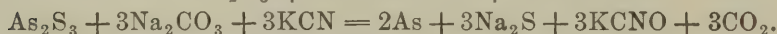
Used as an antidote in case of poisoning.

4. $(\text{NH}_4)_2\text{S}$ precipitates As_2S_5 only in acid solutions, soluble in excess, as $(\text{NH}_4)_3\text{AsS}_4$.

5. *Ferric salts and fresh ferric hydroxide precipitate yellowish-white $\text{Fe}_2(\text{AsO}_4)_2$* when alkali acetates are added, insoluble in $\text{HC}_2\text{H}_3\text{O}_2$.

"Ammonio-magnesian mixture" precipitates *white* $\text{MgNH}_4\text{AsO}_4$.

7. In the dry way, As, on charcoal, gives white fumes of As_2O_3 ; As_2O_3 volatilizes unchanged. Both give off a garlic odor. When As, or As_2O_3 is heated in a glass tube with charcoal, it gives a steel-gray coating. $\text{KCN} + \text{Na}_2\text{CO}_3$ reduce arsenic from all its compounds.



8. Dry $\text{As}_2\text{O}_3 + \text{NaC}_2\text{H}_3\text{O}_2$, heated in the bulb of a reduction tube, gives arsen-dimethyl oxide or (cacodyl oxide) $\text{As}_2(\text{CH}_3)_4\text{O}$, recognized by its offensive odor.

9. Metallic Cu reduces As_2O_3 from HCl solution as an iron-gray film or crust, Cu_5As_2 . This must be *confirmed*, as Sb, Hg, Ag, Bi, Pt, Pl, and Au are also reduced by copper.

10. Arsenic is *reduced* to the elemental state by hydrogen by several methods and combines with it to form AsH_3 (arsine).*

Arsenious hydride (AsH_3) burns with a *bluish* flame; a piece of *cold porcelain* reduces the temperature, and prevents the oxidation of the arsenic, which is deposited in dark steel-gray spots.

*The hydrogen can be generated by the action of H_2SO_4 on Zn; by the action of NaHO on Zn; by sodium amalgam; by the action of Mg on strong solution of NH_4Cl ; by the action of Al on strong KHO . Phosphates interfere with the tests, in alkaline solutions, by sodium amalgam, Mg, and Al by forming phosphorus hydride. Sulphur and sulphites interfere; also, mercury salts and many organic substances. It is not formed in the presence of oxidizing agents, as free Cl, HNO_3 , etc.

Antimony forms similar spots, but they are distinguished as follows: The arsenic spots are steel-gray to black *lustre*; antimony, velvety-brown to black. The arsenic spots dissolve in sodium hypochlorite; the antimony do not dissolve in the hypochlorite solution. The arsenic spots are soluble in ammonium carbonate, and insoluble in hydrochloric acid; the antimony spots are *insoluble* in ammonium carbonate, and soluble in hydrochloric acid. For other differences, see 117.

Arsenic is distinguished from the bases by the fact that *alkali hydroxides and carbonates* do not precipitate arsenious compounds from solutions.

154. Antimony ($\text{Sb}^{\text{III-V}}$, 122). It is a bluish-white, easily pulverized metal. It fuses at 425°C. , and slowly volatilizes at a white heat. It burns at a red heat, and forms Sb_2O_3 . Its proper solvent is aqua regia. A boiling solution of tartaric acid slowly dissolves precipitated antimony.

Antimony forms two oxides, Sb_2O_3 and Sb_2O_5 , antimonious and antimonie anhydride, and SbCl_3 , and SbCl_5 , each having corresponding salts.

155. Tests:—

Sb_2O_3 (WHITE).

1. SbCl_3 is decomposed by water. The SbOCl is soluble in $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$.

2. H_2S precipitates *orange-red* Sb_2S_3 from acid solutions. The precipitate is soluble in HCl , in alkalies, and in alkaline sulphides.

3. $(\text{NH}_4)_2\text{S}$, the same as No. 2, soluble in excess.

Sb_2O_5 (YELLOWISH).

1. SbCl_5 is decomposed by water. $(\text{H}_2\text{O})_2\text{Sb}_2\text{O}_5$.

2. H_2S precipitates *orange* Sb_2S_5 from acid solutions. The precipitate is soluble in HCl , in alkalies, and in alkaline sulphides.

3. $(\text{NH}_4)_2\text{S}$, the same as No. 2, soluble in excess.

4. AgNO_3 (in the presence of KHO or NaHO) precipitates *black* Ag_4O , insoluble in NH_4HO . The Ag_2O is also precipitated, but is soluble in NH_4HO , and leaves Ag_4O undissolved.

5. KI , in HCl solutions, *yellow color*.

AgNO_3 (in the presence of KHO or NaHO) precipitates *white* AgSbO_3 , soluble in NH_4HO .

KI , in HCl solutions, *dark-brown precipitate of I.*

6. All compounds of antimony are reduced, in the dry way, by $\text{KCN} + \text{Na}_2\text{CO}_3$, on charcoal, to a brittle metallic globule.

7. The same reducing agents can be used with antimony as with arsenic. The differences are stated in No. 153. See also 117 for film tests.

8. KHO , NaHO , NH_4HO , Na_2CO_3 , and $(\text{NH}_4)_2\text{CO}_3$ precipitate from antimonious salts $\text{Sb}(\text{OH})_3$. The precipitate is soluble in an excess of KHO or NaHO in the cold, nearly insoluble in NH_4HO ; soluble in Na_2CO_3 on *heating*.

156. Tin ($\text{Sn}^{\text{II-IV}}$, 118). It is a white metal, fusible at 230°C . It tarnishes but little in the air. Its proper solvent is HCl or aqua regia, being dissolved into stannic and stannous chlorides, according to circumstances.

Tin forms two stable oxides and corresponding salts: SnO stannous oxide, SnO_2 stannic oxide. The stannous compounds are *good* reducing agents; the stannic compounds are feeble oxidizing agents.

157. Tests:—CHLORIDE, SnCl_2 (OUS).OXIDE, SnO (OUS).

1. Stannous sulphide, oxide, hydroxide, phosphate, oxychloride, and oxalate are *insoluble* in water.

2. Alkali hydroxides precipitate *white* $\text{Sn}(\text{OH})_2$, soluble in excess, as with KHO forms K_2SnO_2 ; insoluble in NH_4HO .

Alkali carbonates and BaCO_3 give the same reaction.

3. H_2S and sulphides precipitate *dark-brown* SnS , soluble in HCl, in alkalies; moderately soluble in yellow ammonium sulphide.

4. HgCl_2 precipitates *white* Hg_2Cl_2 , with excess black Hg .

5. $\text{K}_3\text{FeC}_6\text{N}_6$, *white* precipitate.

6. $\text{K}_3\text{FeC}_6\text{N}_6 + \text{FeCl}_3$ gives a precipitate of Prussian blue.

7. AuCl_3 with free HCl or HNO_3 , a *purple* precipitate—“purple of Cassius.”

CHLORIDE, SnCl_4 (IC).OXIDE, SnO_2 (IC).

1. Stannic sulphide, oxide, hydroxide, and phosphate are *insoluble* in water.

2. Alkaline hydroxides precipitate *white* H_2SnO_3 , soluble in excess, insoluble in NH_4HO .

Alkali carbonates and BaCO_3 give the same reaction.

3. H_2S and sulphides precipitate *yellow* SnS_2 , soluble in HCl, in alkalies, alkaline sulphides.

4. HgCl_2 , no precipitate.

5. $\text{K}_3\text{FeC}_6\text{N}_6$, no precipitate.

6. $\text{K}_3\text{FeC}_6\text{N}_6 + \text{FeCl}_3$, no precipitate.

7. AuCl_3 , no precipitate.

8. Tin is reduced by zinc from acidulated stannous or stannic solutions as a gray, spongy mass (Sn).

9. On charcoal, with $\text{Na}_2\text{CO}_3 + \text{KCN}$, tin salts are reduced to globules of Sn.

159. Notes on the separation of Lead and Arsenic Group.

1. The solution should have free mineral acid present, as HCl, to precipitate arsenious sulphide; if too acid, it must be evaporated, or antimonious sulphide is not completely precipitated.

2. The precipitated sulphides are more or less *colored*, and are easily distinguished from sulphur by their heavier specific gravity.

3. Pentad arsenic requires several hours to precipitate it; completely only from hot solutions.

4. The precipitated sulphides are *well washed* before treatment with *ammonium sulphide*. Use the smallest possible quantity of $(\text{NH}_4)_2\text{S}$.

5. Copper sulphide is *slightly soluble* in ammonium sulphide. Copper sulphide is not soluble in Na_2S_2 or K_2S_2 , and they can be used to dissolve out As, Sb, Sn; but they dissolve mercuric sulphide, and should not be used when mercury is present.

6. If silver was not removed in the first group, it may be tested for, in the nitric solution of this precipitate, by HCl. See *separation note*.

7. Beyond general indications, the color of the precipitate affords no safe guidance. A pure yellow indicates arsenic and tetrad tin. If copper is absent, and it is orange-yellow, antimony is apt to be present; if black or brown, it denotes dyad tin (Pt or Au).

8. The sulphides of As, Sb, Sn are sometimes separated by treating the precipitates with $(\text{NH}_4)_2\text{CO}_3$, which dissolves the sulphide of arsenic. The sulphides of antimony and tin, dissolved in boiling HCl (under the hood), evaporate the excess of acid; dilute with water, add Pt and Zn: the Sb will be deposited on Pt; the Sn forms on Zn; sometimes the Sn floats in small fragments. These elements can be confirmed by the tests before described. This method gives good results.

9. Free *nitric acid* decomposes the H_2S , and should be expelled before the H_2S is added.

GROUP III.—IRON GROUP.

160. Those metals which, from neutral or alkaline solutions, are precipitated, by the group reagent *ammonium sulphide*, as sulphides, Fe, Mn, Co, Ni, Zn; as hydroxides, Al and Cr. The *rare elements*: Uranium, indium, thorium, cerium, lanthanum, didymium, titanium, tantalum, niobium, yttrium, erbium, vanadium. The oxides and hydroxides of this group are *insoluble* in water. The hydroxides of Co and Ni dissolve in NH_4HO ; Zn dissolves in excess of any alkali; Al in the fixed alkalies, slightly in NH_4HO . Cr_2O_3 redissolves in cold solution of fixed alkalies; it is again precipitated on boiling this solution. The oxides of Al, Cr, and Fe, after ignition, are difficultly soluble in acids.

The presence of *organic substances*, as tartaric acid, sugar, etc., prevents the precipitation of this group by alkalies. H_2S precipitates only ZnS from acetates of this group. The *free acids* redissolve the other sulphides: $\text{FeCl}_2 + \text{H}_2\text{S} = \text{FeS} + 2\text{HCl}$, the FeS being soluble in HCl. It must be borne in mind that H_2S is a reducing agent, and that it precipitates the “*ous*” sulphides.

$\text{NH}_4\text{HO} + \text{NH}_4\text{Cl}$ (the latter on account of Mg, Mn, and Al) will fully precipitate only Al, Cr, and *ic* Fe.

$(\text{NH}_4)_2\text{S}$ precipitates *all* the metals of this group from alkaline solutions as sulphides (*except Al and Cr*). The *sulphides* of Fe, Zn, Mn, Co, and Ni are soluble in *dilute acids*, which keep them in solution during the *second group* precipitation; but they are *insoluble in water*.

The soluble *carbonates* precipitate the metals of this group: Zn, Co, and Ni as basic carbonates; the “*ous*” Fe and Mn as normal carbonates; the “*ic*” salts of Fe, Al, and Cr as hydroxides.

The soluble *phosphates* precipitate this group. The only phosphates which may occur in a sulphide precipitate are those of Al, Mg, Ca, Cr, Ba, and Sr.

In the dry way, they are not easily reduced on charcoal, Zn being the most easily reduced and volatilized. Co, Ni, and Fe

are reduced to *magnetic oxides*. The most of them give characteristic *beads*; none of them give characteristic *flame reactions*.

161. Iron ($\text{Fe}^{\text{II-III}}$, 56). It forms alloys in *all* proportions with manganese, chromium, tungsten, nickel, cobalt, copper, gold, platinum, aluminum, antimony, silicon, sulphur, phosphorus and arsenic; in *limited* proportions only, with zinc, tin, bismuth, and carbon. It scarcely alloys at all with lead, silver, and mercury. Iron, in the laboratory, forms two important oxides, FeO and Fe_2O_3 , and their corresponding series of salts. HCl is a good solvent for iron.

162. Tests:—

FeO (BLACK).

The chloride is Fe_2Cl_4 .

The sulphate is FeSO_4 .

The ferrous compounds are oxidized to ferric compounds by all oxidizing agents, as Cl , $\text{KClO}_3 + \text{HCl}$, Br , HNO_3 , etc.

Are good *reducing* agents.

The salts, or solution, have a green color.

The oxide, hydroxide, sulphide, carbonate, phosphate, oxalate, borate, cyanide, tartrate, tannate, ferrocyanide, and ferricyanide are *insoluble* in water.

Ferrous sulphate is *insoluble* in alcohol.

Ferrous carbonate and sulphide are formed in the wet way

Fe_2O_3 (REDDISH BROWN).

The chloride is Fe_2Cl_6 .

The sulphate is $\text{Fe}_2(\text{SO}_4)_3$.

The ferric compounds are reduced to ferrous compounds by reducing agents, as H_2S , SO_2 , SnCl_2 , H , etc.

Are moderate *oxidizing* agents.

The solution has a brownish-yellow color.

The sulphite, gallate, borate, hydroxide, oxalate, tannate, phosphate, and ferrocyanide are *insoluble* in water.

Ferric sulphate is soluble in alcohol.

Ferric carbonate and sulphide are *not* formed in ordinary conditions in the wet way.

1. Alkali hydroxides precipitate *white* $\text{Fe}(\text{OH})_2$; NH_4Cl or $(\text{NH}_4)_2\text{SO}_4$ dissolves or prevents its formation.

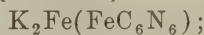
2. Alkali carbonates precipitate *white* FeCO_3 , soon changing to *reddish-brown* $\text{Fe}_2(\text{OH})_6$.

3. H_2S precipitates only the acetate FeS .

4. $(\text{NH}_4)_2\text{S}$ precipitates *black* FeS , finally changing to $\text{Fe}_2\text{O}(\text{SO}_4)_2$.

5. $3\text{FeSO}_4 + 2\text{Na}_2\text{HPO}_4 + 2\text{NaC}_2\text{H}_3\text{O}_2 =$
 $\text{Fe}_3(\text{PO}_4)_2 + 3\text{Na}_2\text{SO}_4 + 2\text{HC}_2\text{H}_3\text{O}_2.$

6. $\text{K}_4\text{FeC}_6\text{N}_6$ precipitates *white* (Everitt's)



changes to Prussian blue in the air.

7. $\text{K}_3\text{FeC}_6\text{N}_6$ precipitates *dark-blue* (Turnbull's)



insoluble in acids.

8. KCNS gives no reaction with ferrous salts.

1. Alkali hydroxides precipitate *reddish-brown* $\text{Fe}_2(\text{OH})_6$, insoluble in alkalis or ammonium salts.

2. Alkali carbonates precipitate $\text{Fe}_2(\text{OH})_6$.

3. $\text{H}_2\text{S} + \text{Fe}_2\text{Cl}_6 =$
 $2\text{FeCl}_2 + 2\text{HCl} + \text{S}.$

4. $(\text{NH}_4)_2\text{S}$ precipitates $\text{FeS} + \text{S}.$

5. $\text{Fe}_2\text{Cl}_6 + 2\text{H}_3\text{PO}_4 + 6\text{NaC}_2\text{H}_3\text{O}_2 =$
 $\text{Fe}_2(\text{PO}_4)_2 + 6\text{NaCl} + 6\text{HC}_2\text{H}_3\text{O}_2.$

6. $\text{K}_4\text{FeC}_6\text{N}_6$ precipitates (Prussian blue) $\text{Fe}_4(\text{FeC}_6\text{N}_6)_3$, insoluble in acid, decomposed by alkalis.

7. $\text{K}_3\text{FeC}_6\text{N}_6$, no precipitate; solution becomes *brown*.

8. KCNS gives *blood-red color*.

9. The beads are described in article 116.

10. $\text{NaC}_2\text{H}_3\text{O}_2$ precipitates, from nearly neutral ferric salt (when heated to boiling and filtered hot), a *basic ferric acetate*; complete separation of all the iron. *Strong* HCl will decompose ferrocyanide of potassium and give a *blue*. This must be borne in mind when testing for iron.

163. Aluminum (Al^{III} , 27.5). It is a silver-white metal, fusible at 700°C . HCl is the best solvent. H_2SO_4 dissolves Al from many of its native compounds. It forms double salts as *alums*. Al_2O_3 with traces of SiO_2 and Fe_2O_3 forms corundum, sapphire, ruby. The Al_2O_3 is employed as a mordant. Organic acids prevent the precipitation of Al as hydroxide or basic salt. Most insoluble salts of Al are changed to soluble compounds by the action of fixed alkali hydroxides. It forms an oxide, Al_2O_3 ; a chloride, Al_2Cl_6 ; a sulphate, $\text{Al}_2(\text{SO}_4)_3$; a nitrate, $\text{Al}_2(\text{NO}_3)_6$. The phosphate, hydroxide, and oxide are the principal *insoluble* compounds.

164. Tests:—

1. Alkali hydroxides precipitate *grayish-white* $\text{Al}_2(\text{OH})_6$, soluble in fixed alkali hydroxides, slightly in NH_4HO , but not if NH_4Cl is present.

2. H_2S does not precipitate it, but $(\text{NH}_4)_2\text{S}$ precipitates $\text{Al}_2(\text{OH})_6$, with escape of H_2S .

3. Alkali carbonates precipitate *white* $\text{Al}_2(\text{OH})_6$ with escape of CO_2 .

4. The *basic acetate* of aluminum is precipitated like 10 in No. 162.

5. Alkali phosphates precipitate *white* $\text{Al}_2(\text{PO}_4)_2$, soluble in fixed alkali hydroxides, but not in acetic acid.

6. For tests in the dry way, see No. 110.

165. Chromium ($\text{Cr}^{\text{II-IV}}$, 52.4). It is a steel-gray metal. The metal is quite rare. Its compounds are *basic* and *acid*. The compounds of Cr are analogous to those of Al .

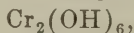
166. Tests:

BASIC.

Cr_2O_3 (BRIGHT GREEN).

1. The phosphate, oxide, and hydroxides are *insoluble* in water. The carbonate and sulphide are not formed in the wet way.

2. Fixed alkali hydroxides precipitate *bluish-green*



soluble in excess on long boiling, or by the addition of NH_4Cl . All Cr is precipitated as $\text{Cr}_2(\text{OH})_6$.

3. H_2S does not affect its solutions, whether acid, neutral or alkaline.

4. $(\text{NH}_4)_2\text{S}$ precipitates $\text{Cr}_2(\text{OH})_6$, with escape of H_2S .

5. Oxidizing agents change it to chromic acid.

6. NH_4HO precipitates $\text{Cr}_2(\text{OH})_6$, slightly soluble in excess.

7. BaCO_3 precipitates $\text{Cr}_2(\text{OH})_6$ with some basic salt.

8. Na_2HPO_4 precipitates $\text{Cr}_2(\text{PO}_4)_2$, insoluble in acetic acid.

9. The most delicate test for Cr, as CrO_3 , is by means of H_2O_2 (hydrogen peroxide) and $(\text{C}_2\text{H}_5)_2\text{O}$ (ether), giving a fine blue color, with one part in 40,000 of water.

ACID.

CrO_3 (SCARLET RED.)

1. It is a powerful oxidizing agent. Its salts are poisonous, and have a metallic taste.

2. Alkali metals form yellow *normal* chromates or reddish *bi-chromates*. Most soluble salts of CrO_3 have permanent forms.

Ba, Pb, Bi, Ag chromates and the *ous* chromates of Mn and Hg are *insoluble* in water.

3. H_2S reduces to *green* solution.

4. $(\text{NH}_4)_2\text{S}$ precipitates (in neutral or alkaline) $\text{Cr}_2(\text{OH})_6$.

5. Reducing agents reduce it to chromic oxide.

6. Lead salts precipitate *yellow* PbCrO_4 , soluble in HNO_3 , insoluble in $\text{HC}_2\text{H}_3\text{O}_2$, difficultly soluble in KHO .

7. Barium salts precipitate *yellow* BaCrO_4 , soluble in HCl and HNO_3 .

8. AgNO_3 precipitates *dark-red* Ag_2CrO_4 , soluble in HNO_3 and in NH_4HO .

10. Tests in the dry way, see Nos. 107, 110, 114, 116.

NOTE.—Fe, Al, and Cr form sesquioxides, R_2O_3 , which may be obtained by igniting their corresponding hydroxides.

167. Cobalt (Co^{II-IV} , 58.6). It is a steel-gray, hard, magnetic metal; does not oxidize in the air at ordinary temperatures. It slowly dissolves in HCl , H_2SO_4 ; readily in HNO_3 . There are two oxides, CoO , cobaltous oxide; Co_2O_3 , cobaltic oxide. The former is a light-brown powder; the latter is black. There are two chlorides, $CoCl_2$ and Co_2Cl_6 . When Co_2O_3 is dissolved in HCl , cobaltic chloride (Co_2Cl_6) is formed; when this is heated, it is converted into cobaltous chloride ($CoCl_2$) with evolution of chlorine.

The cobaltous salts, containing water of crystallization, are red; the anhydrous salts are mostly blue.

The cobaltous salts are generally stable compounds, not easily oxidized; cobaltic salts are very unstable compounds, not permanent in solution, and easily reduced by heat alone to the *ous* state. The cobaltous sulphide, borate, oxalate, phosphate, basic carbonate, hydroxide, cyanide, ferrocyanide, and ferricyanide are *insoluble* in water. Most of these salts form soluble compounds with ammonia. The sulphate is efflorescent; chloride acetate, and nitrate are deliquescent

168. Tests:

1. Fixed alkalis precipitate *blue basic salts*. This absorbs oxygen and becomes *olive-green* hydroxide; if boiled before oxidation in the air, becomes *rose-red* $Co(OH)_2$; does not dissolve in excess. NH_4HO causes the same precipitate, but it is *soluble in excess*.

2. Alkali carbonates precipitate *peach-red* basic salts; on heating, become *violet* and *blue*. They are soluble in excess and in $(NH_4)_2CO_3$.

3. $(NH_4)_2S$ precipitates from neutral, and H_2S , from the acetate, and from the alkaline solutions, *black* CoS, readily soluble in HNO_3 , but best in aqua regia

4. Na_2HPO_4 precipitates *light-red* CoHPO_4 , soluble in acids and in NH_4HO .

5. Oxalates precipitate *reddish-white* CoC_2O_4 , soluble in mineral acids and in NH_4HO .

6. KCN precipitates *brownish-white* CoC_2N_2 , soluble in excess, and in HCl. When boiled with KCN, the precipitate dissolves as $(\text{K}_3\text{CoC}_6\text{N}_6)$, which is not precipitated by NaClO .

7. $\text{K}_4\text{FeC}_6\text{N}_6$ precipitates *grayish-green* $\text{Co}_2\text{FeC}_6\text{N}_6$, insoluble in HCl.

8. $\text{K}_3\text{FeC}_6\text{N}_6$ precipitates *dark-brown* $\text{Co}_3(\text{FeC}_6\text{N}_6)_2$, insoluble in HCl. When to a solution of Co or Ni excess of $\text{NH}_4\text{Cl} + \text{NH}_4\text{HO}$ is added, and then $\text{K}_3\text{FeC}_6\text{N}_6$, a *blood-red color* indicates Co. If Ni is present, and the solution is boiled, a copper-red precipitate forms; if only Co is present, a dirty green, on boiling.

9. $\text{KNO}_2 + (\text{HC}_2\text{H}_3\text{O}_2 \text{ to strongly acid reaction})$, the mixture kept moderately warmed, precipitates *yellow* $\text{K}_6\text{Co}_2(\text{NO}_2)_{12}$, as follows: (Stadtler gives a different formula.)



This reaction separates Co from Ni, as Ni is not precipitated by this reagent.

10. To a dilute solution of cobaltous nitrate, add *tartaric or citric acid*, then an excess of *ammonium hydroxide* and a few drops of potassium ferricyanide; a *deep-red color* appears, even when largely diluted.

11. Tests in the dry way, see No. 116.

169. Nickel ($\text{Ni}^{\text{II-IV}}$, 58.8). It is a bright, hard, malleable, difficultly fusible metal. It is attracted by the magnet. The best solvent is HNO_3 . In nearly all its compounds it closely resembles Co. It forms two oxides, NiO, nickelous oxide, *gray-green*, and Ni_2O_3 , nickelic oxide, black. Both oxides dissolve in acid, and form nickelous salts. The salts of Ni have a *green color*; the anhydrous are *yellow*; the nitrate and chloride are *deliquescent or efflorescent*, according to the moisture in the atmosphere. The

phosphate, oxalate, borate, sulphide, hydroxide, carbonate, cyanide, ferrocyanide, and ferricyanide are *insoluble* in water. Many of these become *soluble* by the action of NH_4HO .

170. Tests:—

1. Fixed alkali hydroxides precipitate *pale-green* $\text{Ni}(\text{OH})_2$, soluble in NH_4HO to *greenish-blue liquid*. NH_4HO precipitates $\text{Ni}(\text{OH})_2$, but it is soluble in *excess* to *blue* color, and it is again precipitated by KHO or NaHO as $\text{Ni}(\text{OH})_2$. The presence of organic acids, sugar, impedes the precipitation by alkalies.

2. Alkaline carbonates precipitate *green basic carbonate* $(2\text{NiCO}_3, 3\text{Ni}(\text{OH})_2)$, soluble in $(\text{NH}_4)_2\text{CO}_3$, or in *excess*, with *blue* or *greenish-blue* color.

3. H_2S and $(\text{NH}_4)_2\text{S}$ precipitate *black* NiS somewhat soluble in NH_4HS .

4. Na_2HPO_4 precipitates *greenish-white* $\text{Ni}_3(\text{PO}_4)_2$, soluble in NH_4HO .

5. $\text{H}_2\text{C}_2\text{O}_4$ precipitates *green* NiC_2O_4 , complete after twenty-four hours.

6. KCN precipitates *pale-green* NiC_2N_2 , soluble in *excess*. When boiled with NaClO, *black* $\text{Ni}(\text{OH})_3$ precipitate. See test No. 6, cobalt.

7. $\text{K}_4\text{FeC}_6\text{N}_6$ precipitates *greenish-white* $\text{Ni}_2\text{FeC}_6\text{N}_6$, insoluble in acids, soluble in NH_4HO , decomposed by fixed alkalies.

8. $\text{K}_3\text{FeC}_6\text{N}_6$ precipitates *greenish-yellow* $\text{Ni}_3(\text{FeC}_6\text{N}_6)_2$, insoluble in HCl.

9. Render the solution of Ni alkaline by NH_4HO , and add a solution of potassium sulphocarbonate*; a deep *brownish-red* fluid is obtained, black by reflected light; when dilute it is pink color—characteristic test for Ni.

10. Tests in the dry way, see No. 116.

* NOTE—The solution is made by taking a five per cent. solution of KHO, saturating one-half with H_2S , adding the other one-half, and then one-twenty-fifth of the volume of CS_2 , digesting at a gentle heat, and separating the dark *orange-red* fluid from the undissolved CS_2 . Keep in a well closed bottle.

171. Manganese ($\text{Mn}^{\text{II-IV}}$, 55). It is a hard, brittle, slightly magnetic, easily oxidized metal. It is related to Zn, Fe, and Cr. It forms the following oxides: MnO , Mn_3O_4 , Mn_2O_3 , MnO_2 , Mn_2O_7 . The first is a powerful *basic* oxide; the last is an acid-forming oxide, yielding HMnO_4 when brought into contact with water. The three intermediate oxides are feebly basic (MnO_2 acts as a weak acid). The chlorides: Manganous, MnCl_2 , light-pink; manganic, Mn_2Cl_6 , brown *liquid*, which readily changes to $2\text{MnCl}_2 + \overline{\text{Cl}_2}$. The sulphates: MnSO_4 , *reddish-yellow* manganous sulphate; $\text{Mn}_2(\text{SO}_4)_3$, *greenish* manganic sulphate.

The higher oxides of manganese dissolve to manganous chloride, with evolution of $\overline{\text{Cl}}$, when heated with HCl ; to manganous sulphate, with evolution of $\overline{\text{O}}$, when heated with H_2SO_4 . The higher compounds of manganese are reduced to *ous* condition from *all* its combinations by boiling with HCl ; the *ous* is the only *stable* form.

MANGANOUS SALTS.

They are rose color, the *oxide* grayish green.

The oxalate, hydroxide, sulphide, phosphate, carbonate, sulphite, and borate are *insoluble* in water. The nitrate, bromide, iodide and chloride are *deliquescent*.

172. Tests:—

1. Alkali hydroxides precipitate *white* $\text{Mn}(\text{OH})_2$; changes in air to brown $\text{Mn}_2\text{O}_2(\text{OH})_2$.

2. $(\text{NH}_4)_2\text{S}$ precipitates (from neutral and alkaline solutions) *flesh-colored* MnS , soluble in HCl and $\text{HC}_2\text{H}_3\text{O}_2$. In the air oxidizes.

3. H_2S does not precipitate *acid* solutions; from *neutral* solutions only *imperfectly*.

4. Na_2HPO_4 (from neutral solutions) precipitates *white* $\text{Mn}_3(\text{PO}_4)_2$; turns brown in air; soluble in dilute acids.

5. Alkali carbonates precipitate *white* MnCO_3 ; *brown* in the air; before oxidation, slightly soluble in NH_4Cl .

6. KCN precipitates *white* MnC_2N_2 , soluble in excess. It darkens in the air.

7. $\text{K}_4\text{FeC}_6\text{N}_6$ precipitates *whitish-red* $\text{Mn}_2\text{FeC}_6\text{N}_6$, soluble in HCl.

8. $\text{K}_3\text{FeC}_6\text{N}_6$ precipitates *brown* $\text{Mn}_3(\text{FeC}_6\text{N}_6)_2$, soluble in acids.

MANGANIC SALTS.

173. Tests:—

1. They are from a *reddish-brown* to *purplish-red* color. The chloride exists only in *solution*. The sulphate is soluble in dilute H_2SO_4 , but is reduced to MnSO_4 by dissolving in H_2O .

2. H_2S and $(\text{NH}_4)_2\text{S}$ *reduce* manganic salts and precipitate MnS . (The $(\text{NH}_4)_2\text{S}$ reduces Mn_2Cl_6 .)

3. The alkali hydroxides and carbonates precipitate $\text{Mn}_2\text{O}_2(\text{OH})_2$.

4. $\text{K}_4\text{FeC}_6\text{N}_6$ precipitates *gray-green* $\text{Mn}_4(\text{FeC}_6\text{N}_6)_3$

5. $\text{K}_3\text{FeC}_6\text{N}_6$ precipitates *brown* MnFeC_6N_6 .

6. The *ic* compounds are changed by heat to Mn_3O_4 .

7. When mixed with H_3PO_4 and evaporated to dryness and heated gently, a violet or blue mass; when heated with H_2O , a *purple-red* phosphate.

8. In the dry way, the *ous* and *ic* act alike; and the *ous* compounds are best identified by *oxidation*, yielding color product. This test can be nicely shown by the electrolysis of a manganese compound in presence of HNO_3 ; when but a trace, gives a pink solution.

9. In the dry way, see 107, 116.

174. Zinc (Zn^{II} , 65). It is a hard, bluish-white metal, brittle at ordinary temperatures; at 94°C . to 149°C ., it becomes ductile and malleable; at higher temperatures, it again becomes brittle. It melts at 411°C . It burns with a bluish-green flame, giving off white fumes, and coats the charcoal with oxide. It

dissolves in HCl and H_2SO_4 , giving off $\overline{\text{H}}$; in HNO_3 with $\overline{\text{NO}}$ or $\overline{\text{NO}_2}$. Pure zinc dissolves very *slowly* in acids or alkalies, unless in contact with Cu or Pt .

The oxide, ZnO , is white; the chloride, ZnCl_2 , is white, deliquescent salt. The carbonate (Smithsonite), ZnCO_3 , occurs native, and is an important ore of Zn ; the sulphate, ZnSO_4 , is isomorphous with MgSO_4 , and strongly resembles it.

The basic carbonate, arseniate, phosphate, oxalate, oxide, sulphide, hydroxide, and ferrocyanide are *insoluble* in water. The most of the insoluble salts are dissolved in alkali hydroxides. The nitrate, iodide, acetate, bromide, chlorate, and chloride are *deliquescent*. The sulphate is *efflorescent*.

175. Tests:—

1. Alkali hydroxides precipitate *white* $\text{Zn}(\text{OH})_2$, soluble in excess of either precipitant; reappears on heating, more readily from NH_4HO than from KHO or NaHO .

2. H_2S precipitates (from neutral or acetic acid solutions) *white* ZnS .

3. $(\text{NH}_4)_2\text{S}$ precipitates (from salts with acids and alkalies) *white* ZnS ; a complete precipitation. It is insoluble in KHO , $\text{HC}_2\text{H}_3\text{O}_2$, and in excess.

4. Alkali carbonates precipitate *white* basic carbonate $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$, soluble in KHO and NH_4HO , sparingly soluble in $(\text{NH}_4)_2\text{CO}_3$.

5. KCN precipitates *white* ZnC_2N_2 , soluble in excess.

6. Na_2HPO_4 precipitates *white* $\text{Zn}_3(\text{PO}_4)_2$, soluble in alkalies, in KHO , in NH_4HO , in strong acids.

7. $\text{K}_4\text{FeC}_6\text{N}_6$ precipitates *white* $\text{Zn}_2\text{FeC}_6\text{N}_6$, soluble in HCl .

8. $\text{K}_3\text{FeC}_6\text{N}_6$ precipitates *brownish-yellow* $\text{Zn}_3(\text{FeC}_6\text{N}_6)_2$, soluble in HCl and in NH_4HO .

9. Tests in the dry way, see 106, 110, 117.

It will be noticed that Zn gives the *only white sulphide*, and that nearly all its precipitates are *white*.

176. Separation of the Iron Group. Phosphates and Oxalates absent.

Boil the filtrate of lead and arsenic groups to *expel* H_2S . Add a few drops of HNO_3 or $(\text{KClO}_3 \text{ plus } \text{HCl})$, and boil an instant to oxidize the Fe; immediately add NH_4Cl , and NH_4HO in excess.

PRECIPITATE.		FILTRATE.	
<p>Co, Ni, Mn, Zn in solution. Add $(\text{NH}_4)_2\text{S}$ and heat gently; filter and wash the precipitate with dilute $(\text{NH}_4)_2\text{S}$, and with H_2O. Treat the well washed precipitate with cold dilute (1 to 12) HCl. If the filtrate is brown, it indicates the presence of Ni.</p>			
PRECIPITATE.		FILTRATE.	
<p>Co, Ni, Mn, Zn in solution. Add $(\text{NH}_4)_2\text{S}$ and heat gently; filter and wash the precipitate with dilute $(\text{NH}_4)_2\text{S}$, and with H_2O. Treat the well washed precipitate with cold dilute (1 to 12) HCl. If the filtrate is brown, it indicates the presence of Ni.</p>			
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NOTE. — In all cases handle quickly and wash thoroughly, and see that the other groups are well washed out. Always test the filtrate, to see that the precipitate is all down.

177. Notes on separation of Iron Group.

1. In many cases when one member of a group is precipitated, it mechanically brings down other members of the group with it; in some cases there is a chemical action of one base with another.

2. The NH_4Cl dissolves manganous hydroxide, and NH_4HO in *excess* dissolves Co, Ni, and Zn hydroxides. To dissolve the Mn, the NH_4HO must be in excess, and the Mn must be in the *ous* condition.

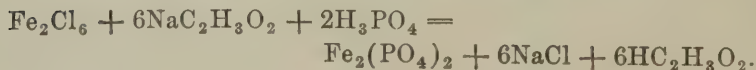
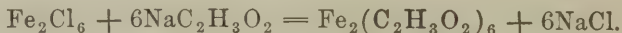
3. If too much HNO_3 is added, manganic compounds may be formed, but enough must be added to oxidize the iron.

4. Organic acids (citric, tartaric) and sugar prevent precipitation by alkalies. They may be removed by heat and HNO_3 . The ignited residue is acidulated with HCl , and carbonaceous matter filtered off.

5. In separating Fe, Al, and Cr by fixed alkalies (KHO or NaHO), they should be *strong enough* to dissolve Al, and the mixture *boiled long enough* to precipitate Cr.

6. In the presence of phosphoric acid, the separation becomes quite difficult. There must be *only free acetic acid in the solution*. It must be strong enough to prevent the precipitation of $\text{Ca}_3(\text{PO}_4)_2$. As it dissolves some ferric phosphate, the separation is not very complete.

7. Fe_2Cl_6 is taken as the reagent, together with $\text{NaC}_2\text{H}_3\text{O}_2$, to neutralize the Cl, as follows:



178. Separation of the Iron Group in the presence of Phosphoric Acid.

Boil the filtrate from Group II. to expel H_2S ; oxidize with a few drops of HNO_3 and boil a short time. Add NH_4Cl and an excess of NH_4HO . Filter, and precipitate by $(\text{NH}_4)_2\text{S}$, and filter. Wash the precipitates separately, digest them together with $(\text{NH}_4)_2\text{S}$, filter and wash.

PRECIPITATES.

FeS , MnS , CoS , NiS , ZnS ; $\text{Al}_2(\text{PO}_4)_3$, $\text{Cr}_2(\text{PO}_4)_3$; $\text{Al}_2(\text{OH})_6$, $\text{Cr}_2(\text{OH})_6$; Ba , Sr , Ca , and Mg phosphates. Dissolve in hot dilute HCl and KClO_3 . Digest to expel free Cl ; filter out the S . Nearly neutralize with dilute solution of Na_2CO_3 , and add solution of $\text{NaC}_2\text{H}_3\text{O}_2$ (strongly acidified with $\text{HC}_2\text{H}_3\text{O}_2$) as long as a precipitate forms. Digest with gentle heat, and filter *while hot*.

PRECIPITATE.

$\text{Fe}_2(\text{PO}_4)_3$, $\text{Al}_2(\text{PO}_4)_3$, $\text{Cr}_2(\text{PO}_4)_3$. Boil the precipitate, for some time, with KHO or NaHO .

RESIDUE.

$\text{Fe}_3(\text{PO}_4)_2$ and $\text{Cr}_2(\text{PO}_4)_3$. Divide into two portions, and treat as directed in No. 176, separation of Cr and Fe .

SOLUTION

$\text{K}_2\text{Al}_2\text{O}_4$ with K_3PO_4 . Acidulate with HCl , and add excess of NH_4HO ; $\text{Al}_2(\text{PO}_4)_3$, not soluble in $\text{HC}_2\text{H}_3\text{O}_2$.

Fuse $\text{Al}_2(\text{PO}_4)_3$ with $1\frac{1}{2}$ parts of SiO_2 plus 6 parts dry Na_2CO_3 ; dissolve in H_2O . Add $(\text{NH}_4)_2\text{CO}_3$ in excess; filter and wash. The residue contains aluminum sodium silicate. The solution, the sodium phosphate.

SOLUTION.

Fe_2Cl_6 , Al_2Cl_6 , Cr_2Cl_6 , or H_3PO_4 ; MnCl_2 , CoCl_2 , NiCl_2 , ZnCl_2 , BaCl_2 , SrCl_2 , CaCl_2 , MgCl_2 .

Add Fe_2Cl_6 , drop by drop, as long as a precipitate forms, and until the liquid becomes red, and heat gently. Filter; test the precipitate for $\text{Fe}_2(\text{PO}_4)_3$. Save the filtrate, and add to it NH_4Cl and NH_4HO ; filter.

PRECIPITATE.

$\text{Al}_2(\text{OH})_6$, $\text{Cr}_2(\text{OH})_6$, $\text{Fe}_2(\text{OH})_6$. Test as in No. 176.

FILTRATE.

To this filtrate add $(\text{NH}_4)_2\text{S}$, and digest and filter.

PRECIPITATE.

MnS , CoS , NiS , ZnS . Separate as in No. 176.

SOLUTION.

May contain Ba , Sr , Ca , Mg . Save this for the next group—Group No. IV.

179. Separation of the Iron Group in the presence of Phosphates. (SECOND METHOD.)

To the filtrate from Group II, add NH_4Cl , and NH_4HO to alkaline reaction; then add $(\text{NH}_4)_2\text{S}$ to complete the precipitation. The filtrate is separated as Group IV.

PRECIPITATE.

FeS , MnS , CoS , NiS , ZnS , S ; $\text{Al}_2(\text{OH})_6$, $\text{Cr}_2(\text{OH})_6$; phosphates of Al , Cr , and of Ba , Sr , Ca , and Mg . Wash the precipitate thoroughly, and treat with cold dilute HCl . If a *black* residue is left, test it for Co and Ni , as in No. 176. SiO_2 is sometimes present in the residue. Filter and boil to expel H_2S ; if turbid, filter again, and *reserve* a small portion of the precipitate, and test for phosphoric acid by $(\text{NH}_4)_2\text{MoO}_4$.

FIRST PORTION.		SECOND PORTION.	
Add a few drops of HNO_3 and boil.		SOLUTION.	
SOLUTION.		PRECIPITATE.	
Fe_2Cl_6 , Al_2Cl_6 , Cr_2Cl_6 , MnCl_2 , $(\text{CoCl}_2, \text{NiCl}_2)$, ZnCl_2 , H_3PO_4 , and BaCl_2 , SrCl_2 , CaCl_2 , MgCl_2 .		BaCl_2 , SrCl_2 , CaCl_2 , MgCl_2 . Add H_2SO_4 and filter.	
1. Test a small portion for iron by KCNS , or test the original solution with $\text{K}_3\text{FeC}_6\text{N}_6$, or $\text{K}_3\text{FeC}_6\text{N}_6$.		BaSO_4 , SrSO_4 , (CaSO_4) . Fuse on charcoal, and dissolve the sulphides in HCl ; and separate as in Group IV.	
2. To the remainder, add Fe_2Cl_6 till a drop is precipitated <i>yellow</i> by NH_4HO (all H_3PO_4 is precipitated), concentrate to a small bulk, add H_2O , nearly neutralize with K_2CO_3 , cool, and add an excess of BaCO_3 ; let the mixture stand, and filter.		SOLUTION. No. 2.	
$\text{Al}_2(\text{OH})_6$, $\text{Cr}_2(\text{OH})_6$, $[\text{Fe}_2(\text{PO}_4)_2]$, $\text{Fe}_2(\text{OH})_6$, BaCO_3]. Boil the precipitate with NaHO or KHO .		Warm and filter.	
PRECIPITATE.		PRECIPITATE.	
$\text{Cr}_2(\text{OH})_6$, $\text{Fe}_2(\text{OH})_6$. Test as directed in No. 176.		Filtrate.	
SOLUTION.		MnS , ZnS . Dissolve in HCl , and separate as in No. 176.	
$\text{K}_2\text{Al}_2\text{O}_4$. Acidify with HCl and add NH_4HO and boil. Precipitate, $\text{Al}_2(\text{OH})_6$.		BaCl_2 , MgCl_2 . Remove Ba , Sr , Ca with H_2SO_4 (Portion 2 above). Precipitate Mg as phosphate. See Group IV.	

GROUP IV.—ALKALINE EARTHS.

180. 1. Those metals whose *carbonates are insoluble in water* are precipitated by the group reagent $(\text{NH}_4)_2\text{CO}_3$ as carbonates, Ba, Sr, Ca, Mg. If much NH_4Cl is present, Mg is not precipitated, but is to be found in Group V., or as a distinct division of the IV. Group (precipitated as phosphate).

2. The group can be precipitated as *phosphates*, if it were not for being so intractable in further operations.

3. The precipitation of Ba, Sr, and Ca by $(\text{NH}_4)_2\text{CO}_3$, in the presence of NH_4Cl , is not very complete; in the presence of NH_4HO , the carbonates are rendered more insoluble.

4. When only one member of the group is present, a solution of CaSO_4 (not too little) precipitates Ba *immediately*, Sr *after some time*, Ca *not at all*.

5. In the above, Ca may be tested by $(\text{NH}_4)_2\text{C}_2\text{O}_4$, *white* CaC_2O_4 . They can also be identified by their flame reactions.

6. The metals of this group are heavier than water, and decompose it; at common temperatures, Mg slowly. Ba, Sr, Ca oxidize in *dry* air, Mg in *moist* air. They dissolve in HCl , H_2SO_4 , HNO_3 with disengagement of H. They combine with Cl, I, Br, O, S, P at elevated temperatures; Mg unites directly with N. Mg burns in the air with dazzling light. The metals of this group are dyads.

7. The *oxides* may be formed by the ignition of their carbonates, nitrates, or any of their salts containing *volatile* acids; or by expelling H_2O from their hydroxides.

8. The *chlorides* are formed by dissolving the oxides, hydroxides, carbonates, sulphides in dilute HCl . Dry Cl converts Ba, Sr, and Ca oxides at a red heat into chlorides (MgO an exception). The chlorides of this group are not decomposed on being heated in a current of H.

9. Ba, Sr, and Ca oxides combine readily with H_2O to form *hydroxides* (MgO combines only slowly). They can also be prepared by boiling their solutions with NaHO . The following is the

order of the solubility of their hydroxides: $\text{Ba}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, the last being almost insoluble in H_2O .

10. The solubility of the sulphates is in the *reverse order* of their hydroxides, BaSO_4 being the most *insoluble*. When the sulphates are heated with carbon, they are converted into sulphides.

11. The nitrates are formed by dissolving the oxides, hydroxides, or carbonates in dilute HNO_3 .

12. The salts of this group are *colorless*, unless the acid is colored.

13. The silicates, carbonates, and normal phosphates are *insoluble* in H_2O .

14. Compounds of Ba, Sr, and Ca moistened with HCl impart characteristic *colors* to non-luminous *flame*. See No. 110.

181. Barium (Ba^{II} , 137). The metal is but little known. It is represented as a yellowish metal. The sulphate, sulphide, chromate, carbonate, iodide, phosphate, oxalate, and silicofluoride are *insoluble* in water.

182. Tests:—

1. Fixed alkali hydroxides precipitate (*only from concentrated solutions*) *white* $\text{Ba}(\text{OH})_2$, soluble in fifty parts of water.

2. Alkali carbonates precipitate *white* BaCO_3 . The precipitation is hastened by heat and by NH_4HO ; it is incomplete in presence of NH_4Cl or NH_4NO_3 . The BaCO_3 is soluble in HNO_3 and HCl, and in 14,137 parts of water.

3. Soluble sulphates (and H_2SO_4) precipitate *white* BaSO_4 , which is but slightly soluble in hot concentrated H_2SO_4 . The BaSO_4 is soluble in 200,000 parts of water.

4. K_2CrO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ precipitate *yellow* BaCrO_4 . The precipitate dissolves in HCl or HNO_3 , and is again precipitated by NH_4HO .

5. Na_2HPO_4 precipitates *white* BaHPO_4 , soluble in acids; reprecipitated by NH_4HO .

6. $(\text{NH}_4)_2\text{C}_2\text{O}_4$ precipitates *white* BaC_2O_4 , slightly soluble in $\text{HC}_2\text{H}_3\text{O}_2$ and in $\text{H}_2\text{C}_2\text{O}_4$, readily in HCl and HNO_3 .

7. H_2SiF_6 precipitates *white* BaSiF_6 , slightly soluble in H_2O , insoluble in $\text{C}_2\text{H}_6\text{O}$.

8. NaIO_3 precipitates *white* $\text{Ba}(\text{IO}_3)_2$, soluble in 1,746 parts of water. Other members of the group do not give this precipitate.

9. Flame reactions, see No. 110.

183 Strontium (Sr^{II} , 87). The color is yellow, somewhat darker than that of Ca. The SrO is a grayish-white powder; the $\text{Sr}(\text{OH})_2$ is about the same color.

The hydroxide is less soluble, the sulphate and chromate more soluble than the corresponding Ba compounds. The chloride is slightly *deliquescent*; the nitrate and acetate, *efflorescent*.

184. Tests:—

1. NaHO , NH_4HO , Na_2CO_3 , $(\text{NH}_4)_2\text{CO}_3$, Na_2HPO_4 form precipitates which *closely resemble* those produced by these reagents with Ba salts.

2. H_2SiF_6 gives no precipitate; neither does $\text{K}_2\text{Cr}_2\text{O}_7$ until enough KHO is added to its solution to convert it to K_2CrO_4 . The K_2CrO_4 slowly precipitates SrCrO_4 , soluble in acetic acid; reprecipitated by KHO .

3. $(\text{NH}_4)_2\text{C}_2\text{O}_4$ precipitates *white* SrC_2O_4 , soluble in HCl and HNO_3 , sparingly soluble in $\text{H}_2\text{C}_2\text{O}_4$ and $\text{HC}_2\text{H}_3\text{O}_2$.

4. Flame reactions, see No. 110.

185. Calcium (Ca^{II} , 40). The metal has a light-yellow color. Calcium *oxide* is quick lime; calcium *hydroxide* is slaked lime. The oxalate, phosphate, and carbonate are *insoluble* in H_2O . The iodate, sulphate, sulphite, and hydroxide are insoluble in $\text{C}_2\text{H}_6\text{O}$, and slightly soluble in H_2O . The nitrate, chloride, and iodide are soluble in $\text{C}_2\text{H}_6\text{O}$. The bromide, iodide, chloride, nitrate, and chlorate are *deliquescent*.

186. Tests:—

1. Fixed alkali hydroxides precipitate *white* $\text{Ca}(\text{OH})_2$, soluble in 700 parts of H_2O

2. Soluble carbonates precipitate CaCO₃; alkaline phosphates precipitate CaHPO₄; ammonium oxalate precipitates CaC₂O₄. The precipitates are similar to those of Ba and Sr.

3. H₂SO₄ (not CaSO₄) precipitates *white* CaSO₄, soluble in a concentrated solution of (NH₄)₂SO₄; distinction from Ba and Sr.

4. K₂Cr₂O₇ or H₂SiF₆ do not give a precipitate (distinguished from Ba).

5. Neutral alkaline *sulphites* (Na₂SO₃) precipitate CaSO₃, soluble in HCl and in HNO₃ and H₂SO₃.

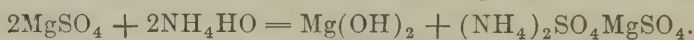
6. Alkaline arsenites precipitate CaHAsO₃, soluble in acids and NH₄HO. The other members of the group give this precipitate only in *concentrated solution*. The precipitate forms slowly, and salts of ammonia must be absent.

187. Magnesium (Mg^{II}, 24). The metal has the color of silver. The carbonate, hydroxide, phosphate, and arseniate are *insoluble* in water; the tartrate, sulphite, and oxalate are sparingly soluble in water. The hydroxide and carbonate are soluble in *ammonium salts* (except (NH₄)₃PO₄). The iodide, nitrate, acetate, chlorate, bromide, chloride are deliquescent.

188. Tests:—

1. The *fixed alkalis* and the other *alkaline earths* precipitate Mg(OH)₂, soluble in ammonium salts.

2. NH₄HO precipitates some of Mg as Mg(OH)₂, leaving the rest as a double salt of Mg and NH₄HO, as for example:



3. K₂CO₃ or Na₂CO₃ precipitates basic Mg₄(CO₃)₃(OH)₂; boiling promotes the precipitation; ammonium salts prevent the precipitation.

4. (NH₄)₂CO₃ precipitates (in concentrated solutions) MgCO₃. The addition of NH₄HO promotes separation, while NH₄Cl prevents the precipitation.

5. Na₂HPO₄ precipitates (if not too dilute) MgHPO₄; promoted by stirring with glass rod. In H₂O, containing NH₄HO, it is soluble in 44,000 parts of water.

6. H_2SO_4 , 2HFSiF_4 , and K_2CrO_4 do not produce a precipitate of Mg salts.

7. $(\text{NH}_4)_2\text{CrO}_4$ produces (in concentrated solutions) MgCrO_4 . NH_4Cl with NH_4HO interferes with the formation of the precipitate.

8. Na_2HAsO_4 precipitates MgHAsO_4 , soluble in acids, even acetic acid.

9. Tests in the dry way, see No. 110.

189. Separation of the Alkaline Earths—Group IV.

METHOD I.

Boil the ammonium sulphide filtrate from Group III., to decompose the ammonium sulphide.

Add $\text{NH}_4\text{Cl} + \text{NH}_4\text{HO} + (\text{NH}_4)_2\text{CO}_3$.	
PRECIPITATE.	FILTRATE.
BaCO_3 , SrCO_3 , CaCO_3 .	
Add $\text{HC}_2\text{H}_3\text{O}_2$; solution as <i>acetates</i> . Now add $\text{K}_2\text{Cr}_2\text{O}_7$.	
PRECIPITATE.	FILTRATE.
<i>Yellow</i> BaCrO_4 . Dissolve in HCl ; flame <i>green</i> . Add H_2SO_4 , <i>white</i> BaSO_4 ; insoluble in acids.	$\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2$, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ [$\text{K}_2\text{Cr}_2\text{O}_7$]. Make alkaline with NH_4HO , and add $(\text{NH}_4)_2\text{CO}_3$.
	PRECIPITATES
	SrCO_3 , CaCO_3 . Wash well, to remove K_2CrO_4 ; dissolve in $\text{HC}_2\text{H}_3\text{O}_2$.
	SOLUTION.
	$\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2$, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$. Add K_2SO_4 (1 to 200 <i>parts</i> of H_2O).
PRECIPITATE.	FILTRATE.
SrSO_4 . Add HCl . Test by flame; crim- son.	CaSO_4 . Add $(\text{NH}_4)_2\text{C}_2\text{O}_4$, <i>white</i> CaC_2O_4 ; test by flame; brick-red.
	$\text{MgCO}_3 + \text{NH}_4\text{Cl}$.
	MgCO_3 , K_2CO_3 , LiCO_3 , Na_2CO_3 , and $(\text{NH}_4)_2\text{CO}_3$.
	Test a separate por- tion for Mg by $(\text{NH}_4)_2\text{HPO}_4$.
	PRECIPITATE
	Of MgHPO_4 . Con- vert to $\text{Mg}(\text{NO}_3)_2$; test by $\text{CO}(\text{NO}_3)_2$; pink mass. See No. 110.

NOTE.—If $(\text{NH}_4)_2\text{HPO}_4$ is added to the filtrate, the MgHPO_4 is precipitated and the alkali metals converted into phosphates. The phosphoric acid may be removed by acetate of lead, and the lead removed by (H_2S) hydrosulphuric acid. Boil, to get rid of H_2S , and filter, if required.

190. Separation of the Alkaline Earths—Group IV.**METHOD II.**

The group is precipitated as in METHOD I., by NH_4HO , NH_4Cl , and $(\text{NH}_4)_2\text{CO}_3$.		
The BaCO_3 , SrCO_3 , CaCO_3 . Dissolve in HCl ; evaporate to dryness on water bath; pulverize and treat with <i>absolute</i> alcohol; filter and wash with alcohol.		FILTRATE.
RESIDUE.	FILTRATE.	
	<p>BaCl_2. Dissolve in H_2O and with H_2SO_4; test by flame; greenish color.</p> <p>SrCl_2 and CaCl_2. Evaporate to dryness, dissolve in H_2O, and precipitate with $(\text{NH}_4)_2\text{CO}_3$; wash and dissolve in HNO_3. Evaporate to dryness, powder, and treat with <i>absolute</i> alcohol; filter and wash with alcohol.</p>	
	RESIDUE.	FILTRATE.
	$\text{Sr}(\text{NO}_3)_2$. Test by flame; carmine.	$\text{Ca}(\text{NO}_3)_2$. Test by flame; brick-red. Also by $(\text{NH}_4)_2\text{C}_2\text{O}_4$.
	FILTRATE. METHOD II.	
	<p>SrCl_2 and CaCl_2. Add a few drops of H_2SO_4. Precipitates SrSO_4 and CaSO_4. Treat with $(\text{NH}_4)_2\text{SO}_4$ + a little NH_4HO.</p>	
	RESIDUE.	SOLUTION.
	SrSO_4 . Test as before.	CaSO_4 . Test as before.

MgCO_3 , etc.
Treat as in Method I.

191. Notes on the separation of Group IV.

1. The NH_4Cl is added to form a double salt with Mg that is very soluble and *not* precipitated with $(\text{NH}_4)_2\text{CO}_3$; NH_4HO is added to make alkaline to litmus; it is now gently warmed and $(\text{NH}_4)_2\text{CO}_3$ added.

2. The *absolute* alcohol dissolves but a small portion of BaCl_2 .

3. The NH_4HO is added to render the carbonates more *insoluble*. The carbonates of Ba, Sr, and Ca are all slightly soluble in NH_4Cl . Those of Ba and Ca are more soluble than Sr.

4. The separation by the first method depends upon the fact that the BaCrO_4 is *insoluble* in dilute acetic acid, while the chromates of Sr and Ca are soluble in that liquid; also upon the fact that SrSO_4 is *almost insoluble* in acidulated solutions, while CaSO_4 is sufficiently soluble to be kept in solution.

5. If the Mg is precipitated by $(\text{NH}_4)_2\text{HPO}_4$, the NH_4HO may be gotten rid of by heat, and the H_3PO_4 as described under Method I. If Na_2HPO_4 is used, you add Na to your solution, which would be an important consideration in making an analysis of the *residue in water analysis*.

GROUP V.—ALKALIES.

192. The members of this group (K, Na, Li, and NH_4), the chlorides, sulphides, and carbonates, *are soluble in water*, and *are not precipitated by the group reagents* HCl , H_2S , $(\text{NH}_4)_2\text{S}$, $(\text{NH}_4)_2\text{CO}_3$. The rare metals of this group are Li, Rb, Cs. The members of this group decompose water (exception NH_4). They are all monads, and strongly electro positive, in this order: Cs, Rb, K, Na, and Li; Cs being strongest. They combine directly with Cl, Br, I, S, etc.

193. Tests:—

1. The hydroxides of Al, Cr, Zn, Pb, Sn, and Sb dissolve in the fixed alkalis. The oxide of Ag and the hydroxides of Cu, Zn, Ni, and Co dissolve in volatile alkali.

2. The chlorides of the fixed alkali metals color a non-luminous *flame*, and give well-defined *spectra* with the spectro-scope.

3. Alkali hydroxides precipitate all non-alkali metals as hydroxides (except Hg, Ag, Sb). NH_4HO does not precipitate Ba, Sr, Ca.

4. The hydroxides and normal carbonates of the alkali metals are not decomposed by *heat* alone.

5. The *oxides* may be obtained by burning the metal in oxygen.

6. The *hydroxides* are prepared by heating carbonates with Ca(OH)_2 until the clear solution no longer effervesces with HCl . A current of Cl passed into their solutions converts them into *hypochlorites* or *chlorates*.

7. The *sulphides* are formed by passing H_2S into their solutions to saturation.

8. The *chlorides* are formed by dissolving the alkalies, or their carbonates, in HCl . When dissolved in HNO_3 , *nitrates* are formed; when dissolved in H_2SO_4 , *sulphates* are formed.

9. The sparing solubility of lithic phosphate and carbonate in H_2O renders it nearly allied to Mg .

194. Potassium (K^I , 39). It has a bluish-white color, and a specific gravity of .865. It melts at 62.5°C .

The platinic chloride, acid tartrate, silico-fluoride, phosphomolybdate, tri-nitrophenate, and perchlorate are but slightly soluble in water. The above list and the carbonate and sulphate are insoluble in alcohol. None of the salts are *absolutely insoluble* in water.

195. Tests:—

1. De Koninck test: * *yellow* precipitate, $6\text{KNO}_2, \text{Co}_2(\text{NO}_2)_6$. The addition of a few drops of acetic acid hastens the reaction.

2. PtCl_4 with HCl precipitates *yellow* crystalline $(\text{KCl})_2\text{PtCl}_4$; evaporate to dryness on the water bath. The precipitate is not dissolved by alcohol.

3. $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ or $\text{NaHC}_4\text{H}_4\text{O}_6$ precipitates *white* granular $\text{KHC}_4\text{H}_4\text{O}_6$. Alcohol promotes precipitation.

* De Koninck test: $6\text{NaNO}_2, \text{Co}_2(\text{NO}_2)_6$ (sodio-cobaltic nitrite). Dissolve ten grams of NaNO_2 and four grams $\text{Co}(\text{NO}_3)_2$, in separate portions of H_2O , and mix; add two C. c. of $\text{HC}_2\text{H}_3\text{O}_2$, and make up to one hundred C. c. The presence of Mg , Ca , Ba , Sr , Fe , Zn , Al does not interfere with this reagent. NH_4HO , Rb , and Cs form precipitates similar to potassium. This test is more delicate than PtCl_4 .

4. Tri-nitrophenic acid (No. 20) precipitates *yellow* $\text{KC}_6\text{H}_2(\text{NO}_2)_3\text{O}$; insoluble in alcohol. The dried precipitate explodes when heated.

5. H_2SiF_6 produces a transparent colorless precipitate, as follows:



6. Flame reaction *violet*. See No. 110.

196. Sodium (Na^I , 23). It is bluish white. Specific gravity, .985. It melts at 95.5°C .

The metantimoniate and silico-fluoride are *sparingly soluble* in water. The acetate, phosphate, sulphate, sulphite, and carbonate are *efflorescent*. The nitrate, hydroxide, and chlorate are *deliquescent*.

197. Tests:—

1. KSbO_3 (in neutral or alkaline solutions) precipitates *white* NaSbO_3 . The reagent should be dissolved as wanted; it is not permanent in solution.*.

2. $(\text{NaCl})_2\text{PtCl}_4$ crystallizes from its *concentrated* solutions in *red* prisms.

3. A crystal of red potassium bichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), illuminated by this *yellow flame* so as to transmit or reflect its light, appears colorless. Paper coated with mercuric iodide, HgI_2 appears *white*; blue cobalt glass, or a solution of indigo, causes the *yellow flame* to disappear.

4. H_2SiF_6 precipitates *white* Na_2SiF_6 ; difficultly soluble in water.

5. Flame reaction *yellow*. See No. 110.

* Metantimoniate of potash (KSbO_3) is made by fusing antimonie acid with large excess of potassium hydroxide, dissolving, filtering, evaporating, and digesting syrupy solution in a silver dish with large excess of potassium hydroxide, decanting the alkaline liquor and stirring the residue to granulate; then dry. It cannot be used in *acid solutions*.

198. NH_4HO (see No. 30). It is tested by its *odor*; by litmus paper, *blue*; the same action on red logwood; blackening mercurous salts; forming white, solid fumes with HCl .

199. Tests:—

1. Nessler's test:* $(\text{KI})_2\text{HgI}_2$ produces a *brown* precipitate of NH_2HgI . This is a very delicate test.

2. HgCl_2 forms "white precipitate," NH_2HgCl .

3. AgCl is dissolved by NH_4HO . (Applicable in the absence of iodides, bromides, thiosulphates, sulphocyanides.)

4. PtCl_4 and $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ form precipitates like those of K in form, color, and solubility.

5. Sonnenschein's reagent† precipitates from neutral or acid solutions NH_4HO —from very dilute solutions; from concentrated solutions it precipitates all the fixed alkalies, except Na and Li .

6. It forms *explosive compounds* with $\text{Cl} = (\text{NCl}_3)$, and $\text{I} = (\text{NH}_2\text{I})$, as follows: $2\text{NH}_3 + \text{I}_2 = \text{NH}_4\text{I} + \text{NH}_2\text{I}$.

200. Lithium (Li^1 , 7). The lightest solid element. Specific gravity, .589. Melts at 180°C . It is the least oxidizable of the alkalies. It is found widely distributed in nature—in mineral waters, ashes of plants, in the analysis of minerals (spodumene, petalite, and lepidolite). The silico-fluoride, carbonate, and phosphate are *sparingly soluble* in water. Many of its salts (chlorate and chloride) are very *deliquescent*.

* To a solution of HgCl_2 add solution of KI till the precipitate is nearly all redissolved; then add solution of KHO ; let stand until the liquid becomes clear; decant. Use the clear solution. Keep from the air when not in use.

† Sodium phosphomolybdate for NH_4HO and acid solutions of the *alkaloids* is made by taking the yellow precipitate formed when mixing acid solutions of ammonium molybdate and sodium phosphate. This precipitate is well washed and heated with sodium carbonate until completely dissolved. Evaporate to dryness, and gently ignite till all the NH_4HO is expelled, Na being substituted for NH_4HO . If it blackens, it is heated with HNO_3 . It is dissolved with H_2O and HNO_3 to strong acid reaction. Solution 1 to 10 parts of H_2O . Keep from vapors of NH_4HO .

201. Tests:—

1. Na_2HPO_4 precipitates Li_3PO_4 ; soluble in 2,530 parts of water; more soluble in ammonium salts (while Mg is less soluble.) The precipitate is hastened by boiling.

2. Nitrophenic acid (see No. 20) forms a yellow precipitate, quite insoluble in water.

3. Na_2CO_3 precipitates *white* Li_2CO_3 ; slightly soluble in H_2O .

4. Flame reaction of LiCl is carmine red. See No. 110.

202. Separation of the Alkalies—Group V.

METHOD I.	METHOD II.
<p>The filtrate from Group IV. may contain K, Na, Li, and NH_4HO. Evaporate a portion to dryness and heat with KHO or NaHO. NH_3 passes off. Test by odor, litmus, and HCl.</p> <p>1. If NH_4HO is present, heat to expel it.</p> <p>2. Precipitate the lithium as phosphate by $(\text{NH}_4)\text{HPO}_4$.</p> <p>3. Get rid of the H_3PO_4 (No. 189, <i>note</i>).</p> <p>4. Separate K and Na by PtCl_4; the 2KCl, PtCl_4 is precipitated; 2NaClPtCl_4 in solution.</p>	<p>1. If NH_4HO is present, heat to expel it.</p> <p>2. Convert K, Na, and Li into platinochlorides (No. 195).</p> <p>3. Dry and extract the Na and Li salts with a mixture of alcohol and ether, containing a little HCl; wash with a mixture six parts of absolute alcohol and one part of ether.</p> <p>4. The residue is K_2PtCl_6; the Li and Na in solution.</p> <p>5. Evaporate to dryness and ignite to reduce the Pt.</p> <p>6. Dissolve in HCl and precipitate the Li as phosphate; Na in solution.</p>

203. Notes:—

1. For traces of NH_4HO , use Nessler's test (No. 199) with the *original solution* before any of the groups are precipitated.

2. As some of the salts of K (as KClO_3 or KNO_3) are added as an oxidizing agent in some of the groups, it is well to test the *original solution* for K.

3. Na is everywhere, and it is not generally added to a mixture of the solutions for *qualitative separation*.

4. The *rare* elements are two *expensive* to give qualitative students. Only *advanced* students should handle them; and they require *special* directions that would be out of place in a book of this kind. I can recommend "*Select Methods*," by William Crookes, second edition, also *Wöhler's Mineral Analysis*, as desirable books for this kind of work.

204. Zettnow* has arranged a scheme without the use of H_2S or $(\text{NH}_4)_2\text{S}$.

The solution (a) may contain salts of: (I.) Pb, Ag, Hg^{I} ; (II.) Ca, Ba, Sr; (III.) NH_4 , Na, K; (IV.) As, Sb, Sn, Hg^{II} , Cu, Cd, Bi; (V.) Fe, Cr, Al; (VI.) Mn, Mg, Co, Ni; (VII.) Zn.

Add HCl to the solution (a); agitate, filter, and wash.

Precipitate (b)— PbCl_2 , AgCl , Hg_2Cl_2 .

Solution (c)—Salts in solution (a), except Ag and Hg^{I} .

1. The Pb in precipitate (b) is separated by hot H_2O and filtration; then precipitate with H_2SO_4 . The Ag is dissolved by NH_4HO , and reprecipitated by HNO_3 , leaving Hg as a *black* residue. See separation of Group I., No. 140. The solution (c) is treated with dilute H_2SO_4 , the precipitate filtered and washed.

Precipitate (d)— CaSO_4 , BaSO_4 , PbSO_4 .

Solution (e)—Classes III., IV., V., VI., and VII. of solution (a).

2. Precipitate (d): The CaSO_4 is in cold water, and precipitated by $(\text{NH}_4)_2\text{C}_2\text{O}_4$. See, also, Ca under filtrate (k). Dissolve PbSO_4 by solution of $(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$ with NH_4HO , and the solution acidulated with $\text{HC}_2\text{H}_3\text{O}_2$ and precipitated by $\text{K}_2\text{Cr}_2\text{O}_7$. The residue contains BaSO_4 and SrSO_4 ; boil with Na_2CO_3 , filter, and wash out Na_2SO_4 ; dissolve the carbonates in HCl, and evaporate to dryness; treat with *absolute alcohol*, and filter. The residue, BaCl_2 , test by flame; also precipitate by solution of SrSO_4 . The solution contains SrCl_2 ; test by flame. A small part of solution (e) is tested for the *alkalies*: NH_4HO is tested by $\text{Ba}(\text{OH})_2$ and boiling; odor. The Ba is removed by $(\text{NH}_4)_2\text{CO}_3$ or dilute H_2SO_4 ; filter. The residue is examined for K and Na. See No. 202.

3. The rest of solution (e) may contain Classes IV., V., VI., VII., As, Sb, Sn, Hg^{II} , Cu, Cd, Bi; Fe, Cr, Al, Mn, Mg, Co, Ni; Zn. The major

* Eyster has a scheme. See *American Chemical Journal*, VII., p. 21-26.

part of solution (e) left with excess of H_2SO_4 from formation of precipitate (d), is treated with Zn and Pt foil in Marsh's apparatus. The gas is tested for As and Sb, or the gas passed into AgNO_3 . See No. 153. The Zn will reduce metals of Class IV. Heat the generating flask ten or fifteen minutes, and filter.

4. Deposit (f): Sb, Sn, Hg, Cu, Cd, Bi.

5. Filtrate (g): Fe, Cr, Al; Mn, Mg, Co, Ni; Zn as sulphates. Deposit (f), well washed, is treated in an evaporating dish with *strong* HNO_3 , and filtered.

6. Solution (h): Nitrates of Hg, Bi, Cu, Cd.

7. Residue (i): Sb_2O_5 , SnO_2 . Test half of solution (h) with SnCl_2 for Hg. To the other half add HCl and boil; then add *excess of* NaHO . The precipitated hydroxides of Bi, Cu, Cd are treated on the filter (after washing) with NH_4HO and NH_4Cl . The Bi is left undissolved;* the Cu and Cd pass into solution. The Cu is recognized by its color and by precipitation with $\text{K}_4\text{FeC}_6\text{N}_6$, after acidulation. The Cd is distinguished from Cu by precipitation by NaHO in ammonical solution.†

Residue (i) is washed, and boiled with HCl, which dissolves the antimonie acid and leaves the metastannic acid undissolved. The solution is tested with Pt and Zn for Sb. The residue is dissolved, with action of nascent hydrogen, made by treating Zn with HCl, and tested with HgCl_2 for Sn.

Treat filtrate (g) with HNO_3 for oxidation. Test a small portion with KCNS for iron (blood red); neutralize with NH_4HO . Treat the remaining portion with BaCO_3 ; filter. In the presence of H_3PO_4 , add Fe_2Cl_6 and digest, before neutralizing and adding BaCO_3 .

8. Precipitate (j): $\text{Cr}_2(\text{OH})_6$, $\text{Al}_2(\text{OH})_6$, with $\text{Fe}_2(\text{OH})_6$ and an excess of BaCO_3 .

9. Filtrate (k): Mn, Mg, Co, Ni; Zn as sulphates.

Precipitate (j) is treated with dilute H_2SO_4 ; precipitates BaSO_4 ; boil to expel CO_2 from the filtrate; add NaHO and boil; oxidize Cr to chromate; test with $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, *yellow chromate of lead*. Treat another part with NH_4Cl in excess to precipitate Al. If NH_4Cl

* The residue is dissolved in HCl, and the solution treated with much H_2O , while BiOCl .

† In case much Cu is present, Cd is tested as follows: The solution is strongly acidulated with HCl, $\text{Na}_2\text{S}_2\text{O}_3$ is added, and then boiled; while hot, it is treated with small additions of $\text{Na}_2\text{S}_2\text{O}_3$, to completion of black precipitate; the liquid is milky with S. After being filtered, test for Cd by NaHO .

is not added in sufficient quantity, Mn, etc., may be precipitated. (See No. 177, notes on separation of Iron Group.)

From filtrate (*k*) get rid of Ba by H_2SO_4 ; filter, and add $(\text{NH}_4)_2\text{CO}_3$ to precipitate MnCO_3 ; filter; test for Mn on Pt foil with $\text{KClO}_3 + \text{Na}_2\text{CO}_3$; *green*. Test for the Ca, which has not been precipitated (*d*) by NH_4HO , then add NH_4Cl and $(\text{NH}_4)_2\text{C}_2\text{O}_4$. To the filtrate add Na_2HPO_4 to precipitate $\text{Mg}_3(\text{PO}_4)_2$. Filter; evaporate to dryness; it may contain Co and Ni. Dissolve in HCl , and separate as in the Iron Group.

Test for Zn by taking a portion of solution (*e*) and treat it with H_2SO_4 and HCl ; filter; heat gently with excess of NaHO and filter. The filtrate contains the Zn as sodium zincate; nearly neutralize with $(\text{NH}_4)_2\text{CO}_3$; treat with NH_4Cl as long as NH_3 escapes; filter. The filtrate is examined for Zn by $\text{K}_4\text{FeC}_6\text{N}_6$.

205. Separation by Electrolysis.

	HNO ₃	H ₂ SO ₄	HCl	KCN	NH ₄ OH	KOH	(NH ₄) ₂ SO ₄ + (NH ₄) ₂ OH	(NH ₄) ₂ S	Na ₂ S	Acetic acid	Acetates, al- kali with KOH	Na ₂ HPO ₄ + KOH	NH ₄ - Ox- alate	K - Oxalate	Tartaric acid	NH ₄ - Tar- trates.	Citric acid	NH ₄ - Citrates	K - Citrate + KOH	Succinic acid	NH ₄ - Suc- cinate	(NH ₄) ₂ CO ₃ + (NH ₄) ₂ OH
Ag.....	Ag	Ag	Pr	Ag	Ag	Pr	Ag	Pr	Pr	Ag	Pr	Pr	Pr	Pr	Ag	Ag	Ag	Ag	Pr	Ag	Ag	Ag
Hg ₂ ^{II}	Hg ^c	Hg ^c	Pr	Pr	Pr	Pr	Pr	Pr	Pr	Pr	Pr	Pr	Pr	Pr	Pr	Pr	Pr	Pr	Pr	Pr	Pr	Pr
Hg ^{II}	Hg	Hg	Hg	Hg	Pr	Pr	Pr	Pr	Pr	Hg	Pr	Pr	Pr	Pr	Hg	Hg	Hg	Hg	Hg	Hg	Pr	Pr
Pb.....	PbO ₂	Pr	Pb	Pr	Pr	Pb	Pr	Pr	Pr	Pb + PbO ₂	Pb + PbO ₂	Pb ^b	Pb [†]	-----	-----	Pb + PbO ₂	Pb + PbO ₂	Pb + PbO ₂	Pb + PbO ₂	Pb	Pb + PbO ₂	Pr
Cu.....	Cu	Cu	Cu	Cu	Cu	Pr	Cu	Pr	Pr	Cu	Pr	Pr	Pr	Pr	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu
Bi.....	Bi ^c	Bi ^c	Bi	Pr	Pr	Pr	Pr	Pr	Pr	Pr	Pr	Pr	Bi [*]	Pr	-----	Bi	Bi	Bi	Bi	Bi	Pr	Pr
Cd.....	Cd	Cd	Cd	Cd	Cd	Pr	Cd	Pr	Pr	Cd ^{ac}	Pr	Pr	Cd [†]	Cd	Cd ^c	Cd	Cd	Cd	-----	Cd	Cd	Cd
As.....	As	-----	As	As	As	-----	As [†]	As [†]	As [†]	As	-----	-----	As [†]	As	-----	As	-----	As	-----	As	As	As
Sb.....	Sb	Sb	Sb	Sb	Pr	Sb	Pr	Sb	-----	Sb	Sb	Sb	Sb [†]	Sb	Sb	Sb	Sb	Sb	Pr	Pr	Pr	Pr
Sn.....	-----	Sn	Sn	Pr	Pr	Sn	Pr	Sn	-----	-----	-----	-----	Sn [†]	-----	-----	-----	Sn	Sn	Sn	Sn	Sn	Pr
Au.....	Au	Au	Au	Pr	Pr	Au	Pr	Pr	Pr	Au	Au	Au	Pr	Pr	Au	-----	Au	Au	Au	Au	Au	Pr
Pt.....	Pt	Pt	Pt	Pt	Pt	Pt	Pt	Pr	Pr	Pt	Pt	Pt	Pt [†]	Pt	Pt	Pt	Pt	Pt	Pt	Pt	Pt	Pr
Mo.....	Mo ₂ O ₃	Mo ₂ O ₃	Mo ₂ O ₃	-----	Mo ₂ O ₃ [*]	-----	Mo ₂ O ₃	Mo ₂ O ₃	Mo ₂ O ₃	Mo ₂ O ₃	-----	-----	-----	-----	Mo ₂ O ₃	Mo ₂ O ₃	-----	Mo ₂ O ₃	Mo ₂ O ₃	Mo ₂ O ₃	Mo ₂ O ₃	Mo ₂ O ₃ [*]
Fe.....	-----	-----	-----	Pr	Pr	Pr	Pr	Pr	Pr	-----	Pr	Pr	Fe [†]	Fe	-----	Fe	Fe	Fe	Fe + Fe ₂ (OH) ₆ [†]	Fe	Fe	Pr
Cr ^{III}	-----	-----	-----	-----	Pr	Pr	Pr	Pr	Pr	-----	Pr	Pr	Cr ₂ (OH) ₆ [†]	-----	-----	-----	-----	-----	Pr	-----	-----	Pr
Cr ^{VI}	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Al.....	-----	-----	-----	-----	Pr	-----	Pr	Pr	Pr	-----	Pr	Pr	Al ₂ (OH) ₆ [†]	-----	-----	-----	-----	-----	-----	-----	-----	Pr
U ^e	U ₃ O ₄ ^d	U ₃ O ₄ ^d	-----	Pr	Pr	Pr	Pr	Pr	Pr	U ₃ O ₄ [†]	Pr	Pr	U ₃ (OH) ₄ [†]	Pr	-----	-----	-----	-----	Pr	-----	U ₃ O ₄	U ₃ O ₄
Mn.....	MnO ₂ [†]	MnO ₂ [†]	MnO ₂	Pr	Pr	Pr	Pr	Pr	Pr	-----	Pr	Pr	MnO ₂ [†]	Pr	-----	-----	-----	-----	-----	-----	MnO ₂	MnO ₂
Zn.....	-----	-----	-----	Zn	Zn	Zn	Zn	Pr	Pr	Zn ^c	Zn	Zn	Zn [†]	Zn	Zn ^c	Zn	Zn	Zn	-----	Zn	Zn	Zn
Co.....	-----	-----	-----	-----	Co	Pr	Co	Pr	Pr	-----	Pr	Pr	Co [†]	Co	Co	Co	Co	Co	CoO	Co	Co	Co
Ni.....	-----	-----	-----	Ni	Ni	Pr	Ni	Pr	Pr	-----	Pr	Pr	Ni [†]	-----	-----	Ni	-----	Ni	NiO	Ni	Ni	Ni
Ba.....	-----	-----	-----	-----	Pr	Pr	-----	-----	-----	-----	-----	-----	Pr	Pr	Pr	-----	-----	-----	-----	-----	-----	Pr
Sr.....	-----	-----	-----	-----	Pr	Pr	-----	-----	-----	-----	-----	-----	Pr	Pr	Pr	Pr	Pr	Pr	Pr	-----	-----	Pr
Ca.....	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	Pr	Pr	Pr	Pr	Pr	Pr	Pr	-----	-----	Pr
Mg.....	-----	-----	-----	-----	Pr	Pr	-----	-----	-----	-----	Pr	-----	Pr	Pr	Pr	Pr	Pr	Pr	Pr	-----	-----	Pr
Na.....	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
K.....	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----

* A. C. J., I., 5. † Classen. a A. P. S., November, 1878. b A. P. S., November, 1887. c A. C. J., VIII., 3. d From neutral. e Uranium solutions should be electrolyzed at about 80°—90° C. on a water bath.

ELECTROLYSIS.

SEPARATION BY ELECTROLYSIS.

206. Any form of battery may be used, or the current from dynamo. The current should be of about such strength as that afforded by two Grove cells. Keep zincs clean and well amalgamated. Let all connections be clean and tight. Use a deep and rather narrow platinum cup to receive the element deposited, in the majority of cases. A shallow platinum dish, however, gives best results for bismuth, and in such few cases where the deposit does not adhere very firmly to the platinum. Use a platinum spiral made of rather heavy wire for the other electrode.

The plus sign (+) over an element, *e. g.*, PbO_2^+ , indicates that the deposition takes place at the positive pole (platinum pole of a Grove cell); the minus sign (—), *e. g.*, Ag^- , indicates that the element separates at the negative (zinc) pole. Pr indicates that the reagent gives a precipitate. A blank space, as under HNO_3 for Fe, indicates that the element is not thrown out of that solution by the current. Whenever a precipitate is formed, filter off before electrolyzing, and convert to a solution, if possible, from which the current will throw out the element.

The following will illustrate the use of the table: A nitric acid solution of Hg, Pb, Fe, Zn, Co is to be separated. Pass current. Hg appears at the — pole; PbO_2 at the + pole; Fe, Zn, Co remain in solution. Remove the liquid to a beaker; add an excess of KOH, filter, and after removing the Hg (by strong HNO_3) from the crucible or platinum dish, place therein the KOH solution of Zn and pass current. Zn separates at the — pole. Dissolve the $\text{Fe}_2(\text{OH})_6$ and $\text{Co}(\text{OH})_2$, formed by KOH, in H_2SO_4 ; add excess of NH_4OH . $\text{Co}(\text{OH})_2$ goes into solution; $\text{Fe}_2(\text{OH})_6$ separates again. Filter; electrolyze the cobalt solution. Co separates at the — pole. Dissolve the $\text{Fe}_2(\text{OH})_6$ in citric or succinic acid and electrolyze. Fe separates at the negative pole.

CHAPTER IV.

SEPARATION OF THE ACIDS.

207. The examination of the bases should always precede the examination of the acids, except H_2SO_4 , HCl , and HNO_3 . The reagents added in the separation of the bases must be borne in mind when testing for the acids, *or the original solution must be examined.*

We may find, while searching for the bases, As_2O_3 , Sb_2O_3 , CO_2 , SiO_2 , CrO_3 , H_2S , H_3PO_4 , $\text{H}_2\text{C}_2\text{O}_4$, H_2SO_3 , and some others.

S, Se, and Te give a hepar on silver coin; H_3P is self-kindling.

Certain bases form with certain acids, compounds insoluble in water. H_2SO_4 forms with Ba, Sr, Ca, and Pb, difficultly soluble sulphates; HCl forms with Ag and Pb, corresponding chlorides; P_2O_5 forms with Ba, Sr, Ca, and Mg, corresponding phosphates. See the *tests* for the bases for example.

Heating separates the acids into two great groups: organic and inorganic. Most of the organic acids blacken when heated to redness; the most noted exceptions are acetic, formic, oxalic, and the volatile organic acids and their salts.

The chlorides of Pb, Ag, Hg, Sn, and Sb, and the sulphide of As are not *easily* decomposed by H_2SO_4 .

CO_2 , SO_2 , H_2S , HCl , HF , and HNO_3 are liberated in the *free* state, while HI , HBr , HCN , CrO_3 , HClO_3 , and $\text{H}_2\text{C}_2\text{O}_4$ are decomposed into *colored* or *colorless* gases.

The reaction may be modified if there is more than one acid in the substance to be examined.

208. If not in the solid state, evaporate the solution to dryness and heat in a small tube with four times its weight of strong sulphuric acid, or bisulphate of potassium.

2. Vapors are evolved.

Indicates

<i>Violet vapors, coloring starch paste blue.....</i>	<i>Iodic acid.</i>
<i>Reddish vapors, coloring starch paste orange...</i>	<i>Bromic acid.</i>
<i>Greenish-yellow explosive gas.....</i>	<i>Chloric acid.</i>
<i>Yellow vapor; smell of chlorine (Cl₂O).....</i>	<i>Hypochlorous acid.</i>
<i>Brownish-yellow, irritating vapors.....</i>	<i>Nitrous and nitric acid.</i>

(b). *Colorless gases.*

With odor of vinegar.....	Acetic acid.
With odor of rotten eggs.....	Hydrosulphuric acid
With odor of burning sulphur.....	{ Sulphurous acid. Thiosulphuric acid.
With odor of peach kernels.....	{ Cyanic acid. Ferrocyanic acid.
With odor of burnt sugar.....	Tartaric acid.
Irritating odor, gives white fumes with NH_3 ...	Hydrochloric acid.
Fuming gas, etches glass.....	Hydrofluoric acid.
Evolves oxygen, changes to brown or green....	Chromic acid.
Odorless, gives turbidity with lime water.....	Carbonic acid.
Burns with blue flame and renders lime water turbid.....	$\text{CO} + \text{CO}_2 = \text{Oxalic acid.}$

Some of these acids are best liberated by mixing the substance with MnO_2 and then treating with H_2SO_4 , or KHSO_4 .

Dilute H_2SO_4 - $\frac{1}{2}$ - Zn colors the fluid—*

Indicates

Violet or lilac.....	Titanic acid.
Blue.....	Tungstic and vanadic acid.
Blue, then green and brown.....	Molybdic acid.
Blue, then muddy or brown.....	Tantallic and niobic acid.
Green.....	Chromic acid.

209. Inorganic Acids. The acids can not be separated into groups with that *accuracy* with which we separate the bases, yet their identification is facilitated by grouping them. If the solution is *acid*, neutralize with NH_4HO ; if alkaline, neutralize with HNO_3 . The *acids* of As, Cr, etc., have been detected as *bases* by H_2S . Many of the bases can be precipitated by *boiling* the solution with an excess of Na_2CO_3 , and filtering. The acids will be present as soda salts. This method should be used *only when time is a consideration*.

210. (1.) BaCl_2 , in the presence of HCl , precipitates sulphuric (H_2SO_4) and hydrofluosilicic (H_2SiF_6) acids.

SULPHUR AND SULPHURIC ACID.

Sulphuric acid dissolves most metals, but is not as generally applicable as HCl or HNO_3 . With evolution of $\overline{\text{H}}$: Zn, Al, Fe, Mn, Sn, Mg; with evolution of $\overline{\text{SO}_2}$: Hg, Ag, Cu, Bi, and Sn. The sulphates of Ba, Pb, Sr, and Ca are insoluble or sparingly soluble in water, and the soluble salts of these elements are used for tests for H_2SO_4 .

Sulphuric acid *liberates most other acids*, and forms sulphates with their bases. The salts of Sn, Hg, Ag, and Sb are *liberated with difficulty*. See No. 22.

Free H_2SO_4 may be detected in sulphates by means of *cane sugar*, as follows: (1) Concentrate the liquid on the *water bath* (in a porcelain dish), add a fragment of white sugar; a greenish-

* Take a small beaker, add the supposed acid; now add H_2SO_4 and Zn as in making H. The nascent H reduces the acid, and changes the color of the solution as above indicated.

black residue indicates H_2SO_4 . (2) The alkaloid, veratrine, gives, with *free* H_2SO_4 (best when heated), a *red* color; more delicate than test No. (1), but more expensive.

211. Tests:—

1. To detect S in albumin, take a solution of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, add NaHO until clear; add the albumin to the solution, and boil (*black colored sulphide*).

2. In the dry way, see No. 107, hepar test.

3. An *alkaline* solution of sulphur with nitroprusside of sodium gives a violet color. See No. 95.

4. In the wet way, see tests under No. 22.

5. The normal sulphates of the alkalies of Ca, Mg, Ag, Mn are *neutral* to litmus paper. The sulphates of the metals of the alkalies, alkaline earths, and PbSO_4 are not decomposed when heated to redness (MgSO_4 an exception). The sulphates of Co, Ni, Cu, Cd, Zn, and Ag require a great heat to decompose them. Sulphates fused with Na_2CO_3 *on porcelain without reducing agents do not stain a silver coin*. See No. 107 (distinction from sulphides).

212. Hydrofluosilicic acid. See No. 15.

213. Tests:—

1. BaCl_2 precipitates white BaSiF_6 .

2. KCl precipitates gelatinous K_2SiF_6 .

3. H_2SO_4 decomposes it, liberating HF , which etches glass. By heat, it is resolved into fluorides and silicon fluorides:



4. NH_4HO in excess precipitates *silicic acid*, with the formation of ammonium fluoride.

5. Heated with microcosmic salt, *no skeleton bead* is formed, because all of the silica volatilizes as SiF_4 .

The Na salts are much like K in No. 2 above, being difficultly soluble.

214. (2.) BaCl_2 in *neutral solutions* precipitates phosphoric (H_3PO_4), boric (H_3BO_3), oxalic ($\text{H}_2\text{C}_2\text{O}_4$), hydrofluoric (HF), carbonic (H_2CO_3), silicic (H_4SiO_4), sulphurous (H_2SO_3), hypsulphurous ($\text{H}_2\text{S}_2\text{O}_3$), arsenious (H_3AsO_3), arsenic (H_3AsO_4), iodic (HIO_3), and chromic acids (H_2CrO_4).

215. Phosphoric acids. There are three modifications, the *ortho*, *pyro*, and *meta phosphoric*, having three, two, and one molecules of H_2O combined with P_2O_5 .

216. Orthophosphates. Tests:—

1. BaCl_2 precipitates *white* BaHPO_4 (from dimetallic phosphates), soluble in HCl and in HNO_3 , sparingly soluble in NH_4Cl .

2. CaCl_2 precipitates (in neutral or alkaline phosphates) *white* CaHPO_4 , soluble in $\text{HC}_2\text{H}_3\text{O}_2$ and in NH_4Cl .

3. "Magnesia mixture" (No. 70) precipitates *white* MgNH_4PO_4 , soluble in NH_4HO , $\text{HC}_2\text{H}_3\text{O}_2$, and slightly soluble in NH_4Cl .

4. AgNO_3 precipitates *light-yellow* Ag_3PO_4 , soluble in HNO_3 and in NH_4HO .

5. $(\text{NH}_4)_2\text{MoO}_4 + \text{HNO}_3$ gives a yellow precipitate of *ammonium phosphomolybdate* of a *variable composition*. The precipitate is soluble in an excess of phosphoric acid, and is prevented by organic substances like tartaric acid.

6. Albumin, or gelatin, *is not* precipitated, nor by solutions of orthophosphates mixed with acetic acid.

7. In the dry way, see No. 107. Dissolve the phosphate in a borax bead, and add tungstate of sodium; *blue* in reduction flame.

8. Fe_2Cl_6 in the presence of a *small* quantity of HCl or HNO_3 and a quite large excess of $\text{NaC}_2\text{H}_3\text{O}_2$ gives a *yellowish-white* gelatinous precipitate of $\text{Fe}_2(\text{PO}_4)_2$; an excess of Fe_2Cl_6 gives a *red color*, and is slightly soluble.

217. Pyrophosphates. Tests:—

1. BaCl_2 fails to precipitate the *free acid*, but precipitates its salts, $\text{Ba}_2\text{P}_2\text{O}_7$; soluble in HCl .

2. AgNO_3 precipitates *white* $\text{Ag}_4\text{P}_2\text{O}_7$, soluble in HNO_3 and in NH_4HO . The precipitate forms best by the addition of an alkali.

3. Ammonium molybdate with nitric acid does not give a precipitate until orthophosphate is formed. *Most* pyrophosphates of the heavy metals (Ag an exception) are soluble in alkali pyrophosphates (distinction from orthophosphates).

MgSO_4 precipitates $\text{Mg}_2\text{P}_2\text{O}_7$, soluble in excess of either solution. NH_4HO fails to precipitate it from these solutions. On boiling, it separates again; by this reaction you can detect *pyro* in the presence of phosphoric acid.

4. White of egg or albumin *is not* precipitated by solution of the acid, nor by a solution of the salts, when mixed with acetic acid.

218. Metaphosphoric acid.

"Magnesia mixture" gives *no precipitate*; albumin *gives a precipitate*. AgNO_3 precipitates *white* AgPO_3 , soluble in alkali metaphosphate solutions; distinction from pyrophosphates. It gives *no precipitate* with ammonium molybdate. Metaphosphates do not coagulate albumin unless acetic is added.

Fusion with Na_2CO_3 converts *meta* and *pyro* into orthophosphates.

219. Boric or boracic acid (H_3BO_3). See No. 4.**220. Tests:—**

1. BaCl_2 and CaCl_2 precipitate *white* $\text{Ba}_3(\text{BO}_3)_2$ and $\text{Ca}_3(\text{BO}_3)_2$.

2. AgNO_3 precipitates *white* Ag_3BO_3 ; normal borates form in part *brown* silver oxide.

3. When the free acid is moistened with glycerin and burned, it gives a *green flame*.

When burned with alcohol, *green flame*.

When moistened with H_2SO_4 , *green flame*.

4. The *free* acid turns turmeric paper *brownish red*, becoming **more** intense when the paper is dried. When mixed with HCl to acid reaction and dried as before, it becomes *red*.

221. Oxalic acid. The oxalic acid is here placed with the inorganic acids. See No. 18.

222. Tests:—

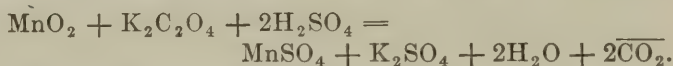
1. H_2SO_4 and heat decompose it into CO , CO_2 , and H_2O . If the mixed gases are passed into NaHO , the CO which escapes burns with a *blue flame*.

2. BaCl_2 precipitates *white* BaC_2O_4 , soluble in HCl or HNO_3 .

3. AgNO_3 precipitates *white* $\text{Ag}_2\text{C}_2\text{O}_4$, soluble in NH_4HO and in hot HNO_3 .

4. All the soluble Ca salts precipitate *white* CaC_2O_4 , soluble in HCl and in HNO_3 , but nearly insoluble in oxalic acid and acetic acid; ammonium hydroxide promotes the precipitation.

5. When the acid or oxalates are mixed with MnO_2 (free from CO_2) + H_2O + a few drops of H_2SO_4 , $\overline{\text{CO}_2}$ escapes:



Oxalic acid is a good *reducing* agent. The oxalates of the **alkaline** metals are soluble in water; the rest are almost insoluble in water. The oxalates of the easily reducible metals, as Ag , Cu , Hg , when roasted, give off CO_2 and leave the metal in the metallic state; the less reducible metals, as Zn , Mg , are left as oxides, and give off CO and CO_2 . Ferrous oxalate is *yellow*.

223. Hydrofluoric acid. See No. 14. The fluorides of the **alkali** metals are soluble in H_2O . The fluorides of the alkaline earths are sparingly soluble in H_2O . The fluorides of Ag , Hg , are readily soluble; of Cu , Zn , Pb , and Fe , sparingly soluble.

224. Tests:—

1. BaCl_2 precipitates *white* BaF_2 , soluble in HCl and HNO_3 .

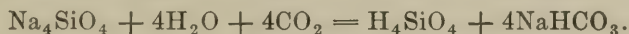
2. CaCl_2 precipitates, after some time, CaF_2 ; NH_4HO hastens the precipitation. It is insoluble in alkaline fluids; slightly soluble in HCl or HNO_3 in the cold. Brazil-wood paper is turned *yellow* by HF .

225. Carbonic acid (H_2CO_3) *has not been isolated*. CO_2 is commonly called carbonic acid. The carbonates of the alkalis are soluble in water. The carbonates of the other metals are insoluble, except a few bicarbonates. All strong acids decompose the carbonates, with effervescence of CO_2 , which *reddens moist litmus paper*. The metallic carbonates are insoluble in alcohol [$(\text{NH}_4)_2\text{CO}_3$ an exception]. The carbonates of the alkalis are not decomposed by heat; the carbonates of the alkaline earths are slowly decomposed at a white heat; all other carbonates are *readily* dissociated. Basic acetate of lead, solutions of $\text{Ba}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$, are delicate tests. See No. 106.

226. Silicic acid. See No. 116, in the dry way. It can be obtained by passing silicic fluoride into water:



or by passing CO_2 into a solution of a soluble silicate:



Silicates are determined by the separation of SiO_2 . Only *alkaline* silicates are soluble in water. Silicic acid is soluble in mineral acids; silicic anhydride is insoluble. When an alkaline silicate is acidulated with HCl (or HNO_3) and evaporated to *dryness* on the water bath, and this operation *repeated* once or twice, the silica is in an *insoluble form as* SiO_2 . See No. 90.

Solutions of alkaline silicates are decomposed by all *acids*. Mix one part of SiO_2 , or a silicate, with two parts of cryolite and four to six parts of H_2SO_4 , in a platinum crucible, and heat *cautiously*, holding near the surface a thick platinum wire, in the loop of which a drop of water is held. A white pellicle of silicic acid is formed on the drop of water.

227. The remaining six acids of this group are *precipitated* or *decomposed* by the group reagents for the *bases*.

Ag GROUP.

H_2SO_3 decomposed by HCl with evolution of $\overline{\text{SO}_2}$.

$\text{H}_2\text{S}_2\text{O}_3$ decomposed by HCl with evolution of $\overline{\text{SO}_2}$ and separation of S.

As GROUP.

H_3AsO_3 precipitated by H_2S as *yellow* As_2S_3 .

H_3AsO_4 precipitated by H_2S as *yellow* As_2S_3 .

HIO_3 decomposed by H_2S with formation of an iodide and separation of S.

Fe GROUP.

H_2CrO_4 precipitated by $(\text{NH}_4)_2\text{S}$ as $\text{Cr}_2(\text{OH})_6$.

228. Sulphurous acid. The sulphites of the alkalies are soluble in water. The normal sulphites of the other metals are sparingly soluble. Sulphurous acid is oxidized to sulphuric acid by the air. It reddens and bleaches litmus. It is a *good reducing agent*. The sulphites are easily decomposed by other acids, liberating $\overline{\text{SO}_2}$ (carbonic, boracic, and, in some cases, hydrosulphuric acids are exceptions).

229. Tests:—

1. BaCl_2 precipitates *white* BaSO_3 , soluble in HCl ; distinction from sulphate.

2. H_2SO_3 and $\text{Zn} + \text{HCl}$ give $\overline{\text{H}_2\text{S}}$. Test by odor.

3. AgNO_3 produces a *white* precipitate, Ag_2SO_3 ; blackens on heating; easily soluble in dilute HNO_3 or in excess of alkaline sulphite.

4. Sulphites, when mixed with $\text{SnCl}_2 + \text{HCl}$, give a yellowish precipitate of SnS_2 .

5. Sulphurous acid $+ \text{HCl}$ and a clean strip of Cu when boiled together, blackens the Cu .

6. Its *reducing action* upon colored salts; as, chromic, permanganic. It decolorizes iodized starch, and the *blue precipitate* with $\text{K}_3\text{FeC}_6\text{N} + \text{Fe}_2\text{Cl}_6$.

7. If a solution of an alkaline sulphite, to which acetic acid is added (just sufficient for acid reaction), and ZnSO_4 , with a small quantity of sodium nitroprusside, the fluid acquires a *red color*; if the quantity is small, the color is hastened by the addition of a small quantity of $\text{K}_4\text{FeC}_6\text{N}_6$. Thiosulphates do not show this reaction.

230. Thiosulphuric or hyposulphurous acid. It does not exist in a free state. Most of its salts are soluble in water. It gives white precipitates with Hg, Pb, and Ag, which soon become yellow, brown, and black. The reactions in general are similar to sulphurous acid.

Since BaSO_4 is insoluble, BaCl_2 separates *sulphates* from sulphites and thiosulphates. CaCl_2 forms a precipitate with sulphite; no precipitate with thiosulphates.

The reactions with HCl and AgNO_3 are different; the HCl liberating SO_2 and S, the silver precipitate being redissolved by thiosulphate, and subsequent blacking of the precipitate. When thiosulphates are treated with iodine, an iodate and a tetrathionate are formed: $2\text{BaS}_2\text{O}_3 + \text{I}_2 = \text{BaI}_2 + \text{BaS}_4\text{O}_6$. Sulphites do not give this reaction.

231. Iodic acid. It is made by the action of HNO_3 , or other oxidizing agent, upon iodine. It is a white crystalline solid. It is decomposed by heat into I and O; it is readily soluble in water. The alkaline iodates are the only salts of this acid which are *freely* soluble in water.

Iodates are decomposed by *reducing* agents. The alkali metals form *acid* iodates.

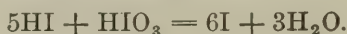
P reduces iodates to iodides; tartaric acid gives a yellow zone when iodates and iodides are together.

232. Tests:—

1. BaCl_2 precipitates *white* $\text{Ba}(\text{IO}_3)_2$, soluble in HNO_3 .
2. AgNO_3 precipitates *white* AgIO_3 , soluble in NH_4HO , but only sparingly soluble in HNO_3 .

3. SO_2 and H_2S decompose it. **Test** for free I by starch or with bisulphide of carbon. An excess of either (SO_2 or H_2S) converts the acid into hydriodic acid.

4. If an iodate and an iodide are mixed and treated with a strong acid, they react upon each other :



Test the *free* iodine.

5. Iodates give off oxygen, and, in some cases, iodine and oxygen. Iodides do not give off oxygen. Morphine reduces iodic acid with separation of iodine. Most of the iodates are insoluble in alcohol; separation from iodides.

6. Salts of lead precipitate *white* $\text{Pb}(\text{IO}_3)_2$.

7. Fe_2Cl_6 precipitates *yellowish-white* $\text{Fe}_2(\text{IO}_3)_6$, soluble in an excess; boiling decomposes it.

233. (3.) Acids precipitated by AgNO_3 and not by BaCl_2 : Hydrochloric (HCl), hydrobromic (HBr), hydriodic (HI), hydrocyanic (HCN or HCy), hypochlorous (HClO), nitrous (HNO_2), hydrosulphuric or sulphuretted hydrogen (H_2S)

234. Hydrochloric acid. See No. 12. Free chlorine is told by the *red color* it gives when added to ferrous salt and potassium sulphocyanate; also by the *blue color* which it gives to a mixture of KI and starch paste. The normal chlorides are soluble in water, except those of the *first group* (Ag , Pb , Hg).

Chlorine gives, with a phosphorous salt bead on a platinum wire, CuO dissolved in it to make it opaque, a *blue colored flame*, due to CuCl_2 .

When a solid chloride is heated with $\text{K}_2\text{Cr}_2\text{O}_4$ + strong H_2SO_4 , a *brown* gas, changing to *red drops*, chlorochromic acid (CrO_2Cl_2). Add NH_4HO in excess, *yellow* $(\text{NH}_4)_2\text{CrO}_4$.

On the addition of an acid, the *yellow* changes to a *reddish-yellow* $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$.

235. Hydrobromic acid. See No. 11.

236. Tests:—

1. AgNO_3 precipitates *yellowish-white* AgBr ; changes to gray; soluble in KCN , sparingly in NH_4HO , insoluble in HNO_3 .

2. HNO_3 decomposes HBr and the bromides (except Ag , Sn , and Hg).

3. $\text{MnO}_2 + \text{H}_2\text{SO}_4 + \text{RBr} = \overline{\text{Br}}$; recognized by its odor.

4. Cl passed through a solution of a bromide, decomposes it, liberates Br and colors it yellow.

5. Bisulphide of carbon, chloroform, or ether, gives, with free Br in solution, *reddish yellow*; free Br colors starch solution *orange yellow*.

6. The *solubility* of the bromides is intermediate between the chlorides and iodides. The general statement can be made, that all bromides are soluble in water, with the exception of the *first group of bases*.

237. Separation of Cl , Br , and I . There are quite a number of methods for separation of Cl , Br , and I .

238. Tests:—

1. A solution of the mixture is placed in a large test tube, a little MnO_2 and water; add one drop of dilute (one to ten) H_2SO_4 . A brown color indicates I . Boil; violet vapors are given off. When these cease, then add 2 C. c. of H_2SO_4 , and boil; brown vapors of Br . Boil till brown vapors cease. When cold, add an equal volume of H_2SO_4 and heat; green vapors indicate Cl .

2. The solvent action of NH_4HO on the chlorides (AgCl , AgBr , AgI) (see No. 135) separates the chlorides from the iodides. A hot, concentrated solution of $(\text{NH}_4)_2\text{CO}_3$ dissolves the chlorides, but only dissolves *traces* of the bromides, and *none* of the iodides.

239. Hydriodic acid. See No. 10.

240. Tests:—

1. A solution of one part of CuSO_4 and two and one-half parts of FeSO_4 precipitates from neutral solution *dirty-white* Cu_2I_2 . The precipitation is hastened by NH_4HO . Chlorides and bromides are not precipitated by this reagent.

2. The CuO bead is similar to the chloride No. 234. The iodides in analysis are identified by liberated iodine.

3. Lead salts precipitate *bright-yellow* PbI_2 .

4. Ozone, chlorine, bromine, nitric acid, sulphuric acid, acidulated potassium nitrite, and chromates, decompose iodides.

5. $\text{MnO}_2 + \text{H}_2\text{SO}_4 + \text{RI} = \text{I}.$

241. Hydrocyanic acid. See No. 13. The solution is feebly acid to test paper. The cyanides of the alkaline earths, alkalies, and mercuric cyanide are soluble in water.

242. Tests:—

1. AgNO_3 precipitates *white* AgCN . The solubility is very like AgCl .

2. Mercurous nitrate ($\text{Hg}^{\text{I}}\text{NO}_3$) precipitates *gray* Hg , and $\text{Hg}(\text{CN})_2$ and $\text{Hg}(\text{NO}_3)_2$ in solution.

3. Copper salts precipitate *yellowish-green* $\text{Cu}(\text{CN})_2$, soluble in an excess of the reagent.

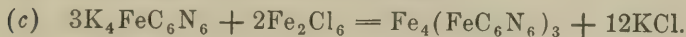
4. Lead salts precipitate *white* $\text{Pb}(\text{CN})_2$, soluble in a large excess of the reagent; precipitated on boiling.

5. HCN in the presence of $\text{K}_4\text{FeC}_6\text{N}_6$. Acidify with H_2SO_4 or $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, shake with ether, which takes up only HCN , but not $\text{K}_4\text{FeC}_6\text{N}_6$. Confirm by other tests.

6. Blood red coloration on heating an alkaline-cyanide solution with picric acid.

7. Soak filtering paper in freshly prepared (three to four per cent.) tincture of guaiacum, let dry, and now moisten it with a one-fourth per cent. solution of CuSO_4 : *blue color* (1 : 300,000).

8. Take a little KHO and FeSO_4 , and warm the mixture for a short time, a very little Fe_2Cl_6 , and the whole *slightly* acidulated with HCl to dissolve the ferrous and ferric hydroxides, when Prussian blue will appear if HCN is present:



9. A solution of HCN is added in excess to one part of KHO and three parts of finely pulverized HgO, which dissolves in a solution of the alkalis *only in the presence of HCN*. This is regarded by Fresenius as a *positive test for HCN*.

243. Hypochlorous acid. See No. 92.

244. Tests:—

1. AgNO_3 precipitates *white* AgCl.
2. Concentrated solutions when boiled give off $\overline{\text{O}}$.
3. $\text{Pb}(\text{NO}_3)_2$ precipitates *white* PbCl_2 ; changes to orange red, and finally brown PbO_2 .
4. MnCl_2 precipitates *dark-brown* $\text{MnO}(\text{HO})_2$.
5. Indigo and litmus solutions are decolorized on the addition of this acid.

All hypochlorites are soluble in water, and are quite unstable, whether solid or in solution.

245. Nitrous acid. See No. 86.

246. Tests:—

1. Dilute H_2SO_4 with iodide of potassium-starch paste: blue color.

2. (a) Acidify with H_2SO_4 , add aniline-sulphuric acid; a few minutes after, a few drops of a *clear* solution of naphthylamin sulphate: *deep red color*. (b) Meta-diamidobenzol: *yellow to brown color*.

3. Evaporate nearly to dryness, and rub with a few drops of a solution of sulphate of aniline, odor of carbohc acid. Carbohc acid gives, with HNO_2 , red, brown, and then green colors.

4. Heat a mixture of one part solution HgNO_3 , one part of carbohc acid (1:100), and three parts H_2O to boiling, and add ten parts of the liquid to be examined; *red color* indicates nitrous acid (1:500,000).

5. Pure HNO_2 is hardly known. Indigo solution is bleached by nitrites. Nitrites liberate iodine from KI, decolorize $\text{K}_2\text{Mn}_2\text{O}_8$ when acidulated with H_2SO_4 . *With very dilute acids*, nitrites form *brown ring*, $2(\text{FeSO}_4)_2\text{NO}$, with a crystal of FeSO_4 . Nitrates do not give these reactions.

The nitrites are *all soluble in water*; AgNO_2 sparingly soluble. Forms *reddish-yellow*, sparingly soluble, $(\text{KNO}_2)_6\text{Co}_2\text{O}_3(\text{N}_2\text{O}_3)_2$. Heated on charcoal, nitrites deflagrate like nitrates.

247. Hydrosulphuric acid (sulphuretted hydrogen). See No. 16. Described under group reagents.

248. (4.) Acids not precipitated by any reagent: Nitric (HNO_3), chloric (HClO_3), and perchloric (HClO_4).

249. Nitric acid. See No. 17.

250. Tests—

1. Molybdic acid with sugar gives *blue color*.
2. Heat one part of carbohc acid and four parts of sulphuric acid: when cold, boil nitrates (as water residue): gives deep-brown to red color.
3. Nascent H and HNO_3 form ammonia.
4. Cu with HNO_3 gives NO_2 , *red fumes*.
5. Nitrates deflagrate on charcoal.

Free nitric acid is distinguished from nitrates by (1) giving the brown with ferrous salt; (2) by coloring woolen threads yellow. A feather can be used as a test in this case. In most cases in nitrates, H_2SO_4 must be used to liberate the HNO_3 .

251. Chloric acid. See No. 81.

252. Tests:—

1. H_2SO_4 decomposes chlorates, $\overline{\text{Cl}_2\text{O}_4}$; *greenish-yellow gas, explosive. Use small quantities.*

2. A solution of a chlorate with H_2SO_4 and a solution of sulphite of soda bleaches indigo. The SO_2 deprives chloric acid of its O, and the liberated Cl bleaches the indigo.

3. Heat chlorate with KCN on Pt foil; violent deflagration ensues. *Use small quantities.*

4. If chlorates are treated with HCl, as follows:



5. Solution of sulphate of aniline (containing toulidin) mixed with two volumes of H_2SO_4 . Intense *blue color* indicates chlorates.

6. All chlorates are soluble in water. Chlorates, when strongly heated, give off oxygen and become chlorides. This reaction enables us to separate chlorates from nitrates by AgNO_3 .

253. Perchloric acid. Tests:—

1. All perchlorates are soluble in water; most of them freely. Potassium salts precipitate *white* KClO_4 , sparingly soluble in water, insoluble in alcohol.

2. Ba and Ag salts are not precipitated.

3. H_2SO_4 (in the cold), HCl, SO_2 fail to decompose the aqueous solution. Indigo is not bleached (difference from all other acids of chlorine).

4. On ignition, perchlorates act like chlorates, but *are more explosive.*

254. Acids identified by ferric chloride (Fe_2Cl_6).

255. Tests:—

(a) *A precipitate is formed.*

1. Hydroferrocyanic, *blue* (in the presence of free HCl). This is decomposed by KHO into Fe_2O_3 and $\text{K}_4\text{FeC}_6\text{N}_6$.

2. Phosphoric acid, *yellowish white*; insoluble in $\text{HC}_2\text{H}_3\text{O}_2$, soluble in HCl , Fe_2Cl_6 , and $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$. If free HCl is present, it should be neutralized by adding $\text{NaC}_2\text{H}_3\text{O}_2$ before adding H_3PO_4 .

3. Tannic acid, *dark blue* (ink). The original compound precipitated by gelatine.

4. In *neutral solutions*, boracic acid *yellowish*; benzoic and succinic acids give *light brown*. Confirm.

(b) A color is produced in the presence of HCl .

5. Hydroferricyanic acid, *brownish*; ferrous salts produce blue precipitate.

6. Sulphocyanic acid, *blood red*; not removed by HCl ; removed by HgCl_2 .

In neutral solutions, the color vanishes on adding HCl .

7. Acetic acid, *reddish brown*. Test ether by making acetic; *i. e.*, add $\text{H}_2\text{SO}_4 + \text{C}_2\text{H}_6\text{O}$, and heat.

8. Formic acid, *reddish brown*. When the original solution is treated with AgO or HgO , $\overline{\text{CO}_2}$ is evolved.

9. Sulphurous acid, *reddish brown*; on boiling, the color vanishes. When HCl is added to the original solution, $\overline{\text{SO}_2}$ is evolved.

10. Meconic acid, *blood red*; unchanged by AuCl_3 .

11. Gallic acid, *black*. The original solution is not precipitated by gelatine.

256. Acids decolorizing indigo solution.

(a) Alone, without addition of an acid.

1. Chlorine, bromine, hypochloric, chlorous, hypochlorous acids, hypochlorites, strong nitric acid, alkaline metallic sulphides, and caustic alkalies.

2. On the addition of HCl or H_2SO_4 , and heating: Chlorates, nitrates, iodates, bromates, manganates, and the *ic* oxides of manganese and lead.

Color water with a *few* drops of indigo solution, and add the substance drop by drop until the change takes place.

257. Separation of some of the Organic Acids.

Remove the metals of the different groups, neutralize the solution with NH_4HO , add CaCl_2 , shake well, and let stand thirty minutes.		
PRECIPITATE.		FILTRATE.
Oxalic and tartaric acids. Wash the precipitate and add cold NaHO , and filter.		
RESIDUE.	FILTRATE.	
CaC_2O_4 . Confirm by No. 222.	$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$. Confirm by No. 260 and No. 24.	
Add to the filtrate three volumes of strong alcohol, and filter.		
PRECIPITATE.		FILTRATE.
Citric, malic, and succinic acids. Wash with alcohol, dissolve in HCl , add NH_4HO , boil, and filter.		
PRECIPITATE.	FILTRATE.	
<i>Calcium citrate</i> . Dissolve in HCl , and test by heating with H_2SO_4 , when CO_2 , CO are given off without darkening; on further heating SO_2 , the mixture blackens. See Nos. 262 and 6.	<i>Malic and succinic</i> . Add alcohol, filter, wash, and dissolve the residue in HNO_3 ; evaporate to dryness on the water bath. Add Na_2CO_3 solution, boil, filter, <i>neutralize</i> with HCl , heat, and add CaSO_4 to a portion: a <i>white</i> precipitate; <i>malic acid</i> . Confirm by No. 265. To the remaining portion add CaCl_2 in excess, filter, add alcohol to the filtrate: a gelatinous precipitate; <i>succinic acid</i> . Confirm by No. 268.	
Benzoic acid and others. Heat to expel alcohol, neutralize <i>exactly</i> with HCl , and add Fe_2Cl_6 ; filter.		FILTRATE.
PRECIPITATE.	FILTRATE.	
<i>Ferric benzoate</i> . Wash the precipitate. Warm with NH_4HO ; in the original solution, evaporate to filter; near dryness. Add HCl and obtain shining crystals of <i>benzoic acid</i> . Confirm by No. 270.		Acetic, formic, etc. Examine for these in the original solution. See No. 278 for acetic; No. 280 for formic.
Uric, gallic, and tannic acids are separately tested. Gallic and tannic can be separated by dialysis.		

258. The common organic acids consist of the following groups: (The organic acids can not be detected with the same certainty as the inorganic acids.)

(1.) Acids precipitated by CaCl_2 in the cold or on boiling: Tartaric acid ($\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ or $\text{H}_2\overline{\text{T}}$), citric ($\text{H}_3\text{C}_6\text{H}_5\text{O}_7$ or $\text{H}_3\overline{\text{C}}$), and oxalic ($\text{H}_2\text{C}_2\text{O}_4$ or $\text{H}_2\overline{\text{O}}$). See No. 221 for oxalic acid.

Malic acid ($\text{H}_2\text{C}_4\text{H}_4\text{O}_5$) is not precipitated by CaCl_2 .

259. Tartaric acid. See No. 24. It occurs in the form of colorless, transparent crystals. It dissolves in hot and cold water; also in alcohol. The solution is acid to litmus paper, and if kept for a short time, becomes mouldy, and decomposes. There are four physical isomers of tartaric acid: Dextro-levulo-racemic, and inactive.

It can be produced artificially by acting upon milk sugar with HNO_3 ; by treating dibromosuccinic ($\text{C}_4\text{H}_4\text{Br}_2\text{O}_4$) with Ag_2O in the presence of H_2O :



HI or iodide of phosphorus converts it into malic or succinic acid. In the presence of oxidizing agents it is converted (usually) into carbonic, formic, and oxalic acids. When fused with KHO, it breaks up into an acetate and an oxalate:



260. Tests:—

1. A cold solution of lime (leaving the reaction alkaline) precipitates white $\text{CaC}_4\text{H}_4\text{O}_6$, soluble in cold solution of KHO; on boiling, it is reprecipitated, dissolves on cooling (distinction from citrate), and is dissolved by acetic acid, while oxalic acid, precipitate of lime, is not. Lime precipitates citric acid *only when heated*.

2. When heated with (one gram with ten C. c. concentrated) H_2SO_4 at 100°C . for forty minutes, citric acid gives yellow color, if one per cent. of tartaric acid is present, a distinct brown shade; more marked with larger proportions.

3. A drop of ferrous sulphate solution added to a solution of tartaric acid, or a soluble tartrate, then a few drops of hydrogen peroxide, and the mixture finally treated with excess of NaHO , a fine *violet coloration* is produced; it is sometimes *almost black*. The color is discharged by SO_2 . Acidulated permanganate or sodium hypochlorite may be substituted for the hydrogen peroxide in the foregoing test, if care be taken to avoid excess, but the results are not so good as with the peroxide.

4. AgNO_3 precipitates *white* $\text{Ag}_2\text{C}_4\text{H}_4\text{O}_6$, soluble in NH_4HO . On boiling, the precipitate turns black; by reduction of silver, gives mirror coating on the glass. The above must be *a normal tartrate and not free tartaric acid*.

261. Citric acid. See No. 6. It forms large, transparent crystals. It is very soluble in hot and cold water, and also in alcohol. The solution is acid to litmus paper, and, like tartaric acid, decomposes on keeping. Heated with KHO , it yields an acetate and oxalate, as follows:



Citric acid chars when heated. The charring is attended with *pungent fumes*, which cannot be mistaken for those of tartaric acid. When citric acid is heated with dilute $\text{H}_2\text{SO}_4 + \text{MnO}_2$, or an acidulated solution of $\text{K}_2\text{Mn}_2\text{O}_8$, it is oxidized with formation of *carbon dioxide and acetone*. Citric acid has been obtained synthetically by many chemists.

262. Tests:—

1. (Citric, succinic, and malic acids.) Precipitate with CaCl_2 , decompose with dilute H_2SO_4 , and boil the filtrate with $\text{K}_2\text{Cr}_2\text{O}_7$: *yellow color* (succinic acid); *green, without odor* (citric acid); *green, with fruity odor*, malic acid.

2. Precipitate tartaric and citric acids by CaCl_2 with a hot and neutral solution of CuCl_2 , when *soluble cupric citrate* and an *insoluble tartrate* remains. Separation.

3. Heat five grams of citric acid with thirty C.C. of NH_4HO for six hours in a sealed tube at a temperature of

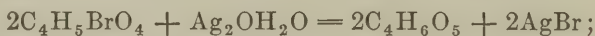
120° C.: yellow color and small crystals are formed. When poured into an evaporating dish and cooled, it becomes *blue*; in a few days, *green*. Malic, oxalic, and tartaric do not interfere with this reaction. Itaconic acid gives the same reaction. One hundredth of a gram of citric acid can be detected.

4. Two grams of the sample of acid are dissolved in twenty C.c. of proof spirit (sp. gr. .920), the solution filtered from any residue, and made up to 45 C.c. with proof spirit; five C.c. of a cold saturated solution of $\text{KC}_2\text{H}_3\text{O}_2$ in proof spirit are added, and the liquid stirred for a few minutes. *The tartaric acid is precipitated as $\text{KHC}_4\text{H}_4\text{O}_6$.* The filtrate contains citric acid; boil off the alcohol, precipitate with lead acetate, remove the lead by H_2S , and determine the free acid.

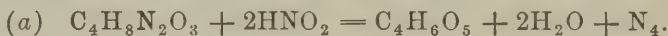
5. CaCl_2 , AgNO_3 , $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. Precipitate citric acid with corresponding citric salts. See tartaric acid.

263. Oxalic acid has been described in No. 221.

264. Malic acid ($\text{H}_2\text{C}_4\text{H}_4\text{O}_5$). It is found in the acids of apples, pears, and various other fruits. Nearly all the malates are soluble in water. It crystallizes with great difficulty. It is acid to litmus paper, and becomes mouldy on keeping. It can be produced artificially by the action of Ag_2O on monobromosuccinic acid



also, by nitrous acid on asparagin, and on aspartic acid:



Fused with KHO it splits up, like tartaric and citric acids, into oxalic and acetic acids. Concentrated H_2SO_4 decomposes the acid and the malates in the solid state with evolution of CO . The mixture blackens only after long boiling.

265. Tests:—

1. Acetate of lead precipitates *white* crystalline $\text{PbC}_4\text{H}_4\text{O}_5$; it comes down better when neutralized by NH_4HO . When

boiled, it melts to a transparent, waxy semi-liquid. It is sparingly soluble in water. If this precipitate is treated with NH_4HO , dried on water bath, pulverized, and moistened with alcoholic ammonia, only malate of ammonium dissolves out when treated with *absolute alcohol* (distinction from tartaric, citric, and oxalic acids). These acids are *insoluble* in the presence of NH_4HO in slight excess when mixed with ten volumes of alcohol, while malate of ammonium goes into solution.

2. AgNO_3 precipitates *white* $\text{Ag}_2\text{C}_4\text{H}_4\text{O}_5$; on boiling, turns gray.

3. When only one of the four acids is present in a solution, lime water precipitates tartaric and oxalic acids *in the cold*; citric acid *on boiling*. Malic acid is not precipitated. Calcium tartrate is soluble in NH_4Cl , whilst the oxalate is not.

NOTE— CaCl_2 precipitates, *in the cold*, tartaric acid from neutral solutions; (2) *by boiling* CaCl_2 , rendered alkaline by $\text{Ca}(\text{OH})_2$, citric acid; (3) not precipitated from hot or cold solutions by CaCl_2 , but is precipitated on adding alcohol to the solution *malic acid*. Oxalic, boracic, phosphoric, hydrofluoric, carbonic, arsenious, and arsenic acids are precipitated from neutral solutions by CaCl_2 ; but these will have been removed before the organic acids are reached.

266. (2.) Acids precipitated by ferric chloride (Fe_2Cl_6), and not by CaCl_2 : Benzoic ($\text{C}_7\text{H}_6\text{O}_2$), succinic ($\text{C}_4\text{H}_6\text{O}_4$) acids, These acids sublime without alteration. They are but little acted upon by HNO_3 .

267. Succinic acid. See No. 34. It is bibasic. It occurs ready formed in amber and in certain lignites. It emits a suffocating vapor below the melting point (180°C.). Fused with KHO , it yields a carbonate and an oxalate, and gaseous hydrocarbons. It can be produced from malic and tartaric acids by acting on them with HI . It is not attacked by concentrated H_2SO_4 . Heated in the air, succinic acid burns with a blue flame, free from soot. Most of the succinates are soluble in H_2O .

268. Tests:—

1. CaCl_2 gives *no precipitate*, but on adding alcohol a gelatinous precipitate of $\text{CaC}_4\text{H}_4\text{O}_4$; soluble in NH_4Cl .

2. Fe_2Cl_6 (in neutral solutions of succinates of the alkali metals) precipitates a *brownish, pale-red*, bulky $\text{FeC}_4\text{H}_4\text{O}_4$, soluble in mineral acids. NH_4HO decomposes it.

3. $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ precipitates *white amorphous* $\text{PbC}_4\text{H}_4\text{O}_4$, soluble in excess of either; in a short time it separates out in a crystalline form.

4. Alcohol, ammonium, and barium chloride produce a *white* precipitate, $\text{BaC}_4\text{H}_4\text{O}_4$.

269. Benzoic acid is monobasic. It is contained in gum benzoin. It volatilizes completely when heated, with partial decomposition, and forms needles; the fumes provoke coughing. When kindled, the crystals burn with a smoky flame. It can be produced artificially by oxidizing bitter almond oil, or by boiling hippuric acid with HCl , or from the washings of wool (*suint*). Benzoic acid is sparingly soluble in cold water, freely soluble in hot water and in alcohol.

270. Tests:—

1. Fe_2Cl_6 precipitates *bulky, flesh-colored* $\text{Fe}(\text{C}_7\text{H}_5\text{O}_2)_3$. NH_4HO decomposes it; it dissolves in a *little* HCl .

2. $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ precipitates (from alkali benzoate, not from free acid) *flocculent lead benzoate*, soluble in excess, insoluble in sodium benzoate.

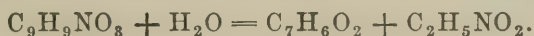
3. A mixture of alcohol, ammonium, and barium chloride, or calcium chloride, produces no precipitate in solutions of benzoic acid or of alkali benzoates.

NOTE—This group of acids can be separated by their solubility. Succinic is *readily soluble* in water; benzoic, *sparingly soluble*. They can be detected by precipitating with Fe_2Cl_6 . Warm the washed precipitate with NH_4HO , filter, concentrate,

and divide into two parts. Add to one part HCl; to another, barium chloride, alcohol, and ammonium.

These acids do not prevent the precipitation of the hydroxides of the heavy metals by alkalies. Benzoic acid from Siam benzoës decolorizes an alkaline solution of $K_2Mn_2O_8$. Acids from other sources alter the color to nearly green.

The student can make benzoic acid by heating putrid cow's urine with lime, filtering, concentrating the filtrate, and precipitating the benzoic acid with an excess of HCl. The hippuric acid of the urine breaks up into benzoic acid and glycocine:



271. (3.) Acids precipitated by $AgNO_3$ in strong neutral solutions: Ferrocyanic ($H_4FeC_6N_6$), ferricyanic ($H_3FeC_6N_6$), sulphocyanic (HCNS), acetic ($HC_2H_3O_2$), and formic (CH_2O_2) acids.

272. Ferrocyanic acid. See No. 8. This acid belongs to both groups, being precipitated by Fe_2Cl_6 .

273. Tests:—

1. $AgNO_3$ precipitates *white* $Ag_4FeC_6N_6$, insoluble in dilute HNO_3 , soluble in KCN.

This has been sufficiently described under No. 8.

$K_4FeC_6N_6$ gives a precipitate with Sb, Al, Bi, Cd, Ca, Co, Cu, Fe (*ous* white then blue), *ic* deep blue; Pb Mg, Mn, Hg (*ous* and *ic*), Mo, Ni, Ag, Sn, U, and Zn. The *ferro* is separated from *ferri* cyanide by the insolubility of alkali salts in alcohol (*ferro* precipitated, *ferri* not precipitated); also by reactions with *ic* and *ous* Fe and with Cu. Ferro is the *ous* cyanide; ferri is *ic* cyanide. Ferrocyanide gives colored reactions with many of the alkaloids.

The above reactions are given in Reactions for Bases and Acids, pages 158, 162, and 164.

274. Ferricyanic acid. See No. 7.

275. Tests:—

1. $AgNO_3$ precipitates *orange* $Ag_3FeC_6N_6$, insoluble in dilute HNO_3 , soluble in KCN.

2. FeSO_4 , *blue precipitate* (Trumbull's blue), $\text{Fe}_3(\text{FeC}_6\text{N}_6)_2$; insoluble in dilute acids.

$\text{K}_3\text{FeC}_6\text{N}_6$ gives precipitates with Bi, Cd, Co, Cu, Fe (*ous*), Mn, Hg (*ous*), Ni, Ag, Sn (*ous*), Zn. See Reactions for Bases and Acids, page 162.

276. Sulphocyanic acid. See No. 21. Sulphocyanates of the metals of the alkalies, alkaline earths, Fe (*ous* and *ic*), Mn, Zn, Co, and Cu, are soluble in water.

277. Tests:—

1. The ferric reaction is the *most distinctive* (blood red).

2. It gives reactions with Co, blue; Cu, black; Fe^{III} , blood red; Pb, yellowish; Hg^{I} , white ("Pharaoh's serpents"); Pt, deep red; Ag, white. It is written HCNS or KCyS.

The *absolute* acid decomposes quite rapidly, with evolution of CO_2 , CS_2 , H_2S , HCN, H_3N , and other products.

278. Acetic acid. See No. 1. It is monobasic. It exists in the juices of many plants, especially of trees. In the liquid state it has a density of 1.063, and boils at 120°C . Its vapor is inflammable. On account of its solidifying below 16° , it has received the name of *glacial acetic acid*, in contra-distinction to a mixture of water and acid, which does not crystallize; this mixture is commonly called acetic acid. It does not redden litmus until mixed with water. The most powerful oxidizing agents attack it with difficulty. Most of the acetates are soluble in water.

Metallic acetates give the following reactions:

1. Subjected to dry distillation, *acetone* is given off; characteristic odor.

2. Heated with As_2O_3 , *odor of cacodylic oxide*; *very poisonous*.

3. Heated with H_2SO_4 , acetic acid is evolved.

4. Neutral solution and ferric chloride (*avoiding excess*) give a deep-red liquid containing ferric acetate. When this is boiled the liquid becomes colorless and *reddish-brown ferric oxyacetate*.

HCl changes the red ferric acetate to *yellow* (difference from sulphocyanate). The metallic acetates are soluble in water; Ag and Hg (*ous*) but sparingly soluble.

279. Formic acid (HCHO_2). It is monobasic. All its salts are soluble in water. It occurs in ants, in caterpillars, and in several secretions of the human body. It is present in the juice of the stinging nettle and other vegetables; in some cases in mineral waters.

It is commonly made by distilling dry oxalic acid with glycerin. Oxydizing agents like Cl, Br, CrO_3 , $\text{K}_2\text{Mn}_2\text{O}_8$, convert it into carbonic acid. It has a penetrating odor, and when concentrated produces intense irritation on the skin.

280. Tests:—

1. Fe_2Cl_6 gives the same reaction as acetate (*blood red*).
2. AgNO_3 precipitates *white* AgCHO_2 ; darkens on standing.
3. HgCl_2 is reduced to Hg_2Cl_2 or *Hg*. Acetates do not give this reaction. *It is a good reducing agent.*
4. When heated with $\text{H}_2\text{SO}_4 + \text{C}_2\text{H}_6\text{O}$, ethyl formate ($\text{C}_2\text{H}_5\text{CHO}_2$); fragrant odor of peach kernels.

5. At a gentle heat, strong H_2SO_4 evolves $\overline{\text{CO}_2}$ from a formate or formic acid. Strong alkalies produce an *oxalate*.

NOTE—To separate acetic from formic acid: Saturate the free acids with slight excess of calcined magnesia or carbonate of lead, filtering, evaporating the filtrate to a small bulk, and adding a large proportion of alcohol. The formates of Mg or Pb are precipitated, while the acetate remains in solution.

281. Acetic, formic, lactic, propionic, and butyric acids may be distilled with water (lactic with difficulty). Acetic and formic acids have been described.

282. Lactic acid ($\text{H}_2\text{C}_3\text{H}_4\text{O}_3$). Four isomeric lactic acids are now believed to exist. *Ordinary* lactic acid is formed by the fermentation of milk, cane, and grape sugars. It is also found in vegetable matters that have turned sour. Sarcosolactic or

paralactic acid exists in muscular flesh. With bases, it forms neutral salts; they are all soluble in water and in alcohol, but are insoluble in ether.

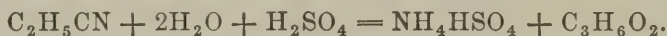
Concentrated lactic acid is a colorless, odorless, syrupy liquid of a very acid taste. Specific gravity, 1.248. Acid containing 75 % has a sp. gr. 1.212. At 130° C. it begins to boil. Lactic acid is miscible in all proportions with water, alcohol, glycerin, and ether, but slightly soluble in chloroform, and insoluble in carbon disulphide and petroleum spirit. It does not reduce Fehling's solution; but it decolorizes $K_2Mn_2O_8$, both in acid and alkaline solutions. Hot HNO_3 converts lactic acid into oxalic acid.

283. Tests:—

1. Calcium lactate under the microscope shows crystalline needles in tufts with short stalks, like double paint brushes. Zinc lactate shows spherical groups of needles.

2. Lactic acid may be separated from those organic acids which form *insoluble lead salts*, as lead lactate is *soluble and remains in solution*; or by barium, as barium lactate is *soluble in alcohol*.

284. Propionic acid ($HC_3H_5O_2$). It is obtained by boiling ethyl cyanide with sulphuric acid:



It separates from its solution in water as an oily layer on the addition of $CaCl_2$. It resembles acetic acid. It has the disagreeable odor of rancid butter and acetic acid. It is contained in crude oil of amber, in sour cocoanut milk, and in certain wines when the fermentation has been pushed too far. It boils at 140° C., and has a density of .996 at 19°. The propionates are all soluble in water.

The free acids are evaporated to dryness with PbO , the residue treated with cold water, and the liquid filtered. Basic *propionate of lead dissolves*, while most of the acetate, formate, and acrylate remains insoluble. If the solution is boiled and stirred quickly, the propionate separates out as a crystalline precipitate.

285. Butyric acid ($\text{HC}_4\text{H}_7\text{O}_2$). There are two isomers, normal butyric and isobutyric acids. The normal butyric acid is a colorless liquid, having the odor of rancid butter and acetic acid. It is soluble in water, alcohol, and ether in all proportions; it is insoluble in concentrated solution of CaCl_2 or NaCl . It may be separated from aqueous solution by saturating the liquid with CaCl_2 , and then agitating with ether. The ethereal layer is allowed to evaporate spontaneously. Also by fractional distillation. All the metallic butyrates are soluble in water. The butyrate of copper forms *bluish-green* monoclinic crystals, while valerianic acid separates in oily drops when treated with copper acetate (*separative*).

The most delicate and characteristic test is the formation of *ethyl butyrate* on heating with alcohol and sulphuric acid. The ether has a *fragrant odor of pine-apple*.

CHAPTER V.

COMPARISON OF THE BASES AND ACIDS.

Reaction of the Bases—Group I. Metals precipitated from their solutions by H_2S .

Reagents.	Silver.	Mercurous.	Mercuric.
Hydrogen Sulphide, (H_2S) Group Reagent.	Black, Ag_2S . Insol. in alkaline sulphides. Sol. in HNO_3 . Ag_2S is soluble in 35,000 parts of H_2O .	Black, HgS . Hg . Insol. in $(NH_4)_2S$, and in HNO_3 . Sol. in potassium sulphide.	First white, then yellow and red brown to black, $HgCl_2 + x HgS$. Insol. in HNO_3 . Soluble in K_2S . Sol. in aqua regia and alkalis. Sol. in 20,000 parts H_2O .
Hydrochloric acid, (HCl)	White, $AgCl$. Light changes it to violet. Insol. in acids. Sol. in NH_4HO , in KCN , and in $Na_2S_2O_3$. Sol. in 1,000,000 parts H_2O .	White, Hg_2Cl_2 . Soluble in HNO_3 , and in aqua regia as $HgCl_2$ —blackened by NH_4HO . Soluble in 12,000 parts boiling H_2O . Sol. in NH_4Cl .	—
Sodium hydroxide, ($NaHO$.)	Light brown, Ag_2O . Sol. in HNO_3 , and NH_4HO . Sol. in 3,000 parts H_2O .	Black, Hg_2O . Sol. in HNO_3 . Insol. in NH_4HO . Insol. in alcohol.	Yellow, HgO . Sol. in 200,000 parts of H_2O —Insol. in alcohol, and NH_4HO .
Ammonium hydroxide, (NH_4HO .)	Light brown, Ag_2O . Sol. in excess—Sol. in HNO_3 , $HC_2H_3O_2$, and NH_4HO .	Black, mercurous-ammonium salts. Sol. in HNO_3 . Insol. in alkalis. [Mercury, silver and gold do not form hydroxides.]	White, mercuriammonium salts. Sol. in HCl , sparingly sol. in NH_4HO .
Sodium Carbonate, (Na_2CO_3 .)	Grayish white, Ag_2CO_3 . Sol. in NH_4HO .	Yellow precipitate basic salt, soon becomes black.	Red brown, basic salt $+ x HgO$. By heating becomes yellow oxide, HgO .
Sulphuric Acid, (H_2SO_4 .)	White, Ag_2SO_4 . Sparingly sol. in excess, and in H_2O .	White, Hg_2SO_4 . Sol. 500 parts H_2O .	—

Group I—Continued.

Lead.	Copper.	Bismuth.	Cadmium.
Black, PbS. Insol. in $(\text{NH}_4)_2\text{S}$. Sol. in HNO_3 .	Brown black, CuS. Sol. in 950,000 parts H_2O . Sol. in HNO_3 , sparingly sol. in $(\text{NH}_4)_2\text{S}$ —Sol. in KCN.	Brown black, Bi_2S_3 . Sol. in HNO_3 —Insol. in KCN.	Yellow, CdS. Sol. in HCl. Insol. in KCN.
White, PbCl_2 . Sol. in 135 parts H_2O —30 parts hot H_2O . Insol. in alcohol, and NH_4HO .	CuCl_2 , freely soluble. Cu_2Cl_2 . Insoluble in H_2O .	BiOCl . Insoluble in H_2O .	—
White, $\text{Pb}(\text{OH})_2$. Sol. in excess. Sol. in HNO_3 . Insol. in NH_4HO .	Blue, $\text{Cu}(\text{OH})_2$ heated becomes black, CuO. Soluble in acids.	White, $\text{BiO}(\text{OH})$. Insol. in excess. Sol. in HCl and HNO_3 .	White, $\text{Cd}(\text{OH})_2$. Insol. in excess. Soluble in acids.
White, $\text{Pb}(\text{OH})_2$. Insol. in excess.	Greenish blue precipitate, basic copper ammonium salts. Sol. in excess with blue color. Sol. in KCy.	White, $\text{BiO}(\text{OH})$. Insol. in excess. Sol. in HCl and HNO_3 .	White, $\text{Cd}(\text{OH})_2$. Sol. in excess, and in NH_4Cl . Sol. in KCy and precipitated from this solution by $(\text{HN}_4)_2\text{S}$.
White precipitate. Basic lead carbonate,	Blue precipitate, basic copper carbonate, when heated becomes black brown. CuO.	White, $(\text{BiO})_2\text{CO}_3$. Insol. in excess. Sol. in HCl, and in HNO_3 .	White, $\text{Cd}(\text{O}_3)$. Insol. in excess—precipitate not complete in presence of NH_4Cl .
White, PbSO_4 . Sol. in 13,000 parts H_2O .	Sol. in $3\frac{1}{2}$ parts H_2O .	—	—

Group I—*Continued.*

Reagents.	Silver.	Mercurous.	Mercuric.
Potassium chromate, K_2CrO_4 .	Dark red, Ag_2CrO_4 . Sol. in HNO_3 , and in NH_4HO .	Red basic chromate. Sol. in HNO_3 .	Yellowish red, $HgCrO_4$. Sol. in HNO_3 .
Potassium ferrocyanide, K_4FeCy_6 .	White, Ag_4FeCy_6 . Insol. in NH_4HO .	White, Hg_2FeCy_6 .	—
Stannous, chloride, $SnCl_2$.	White, $AgCl$.	Dark gray, Hg	White, Hg_2Cl_2 , with excess metallic Hg .
Potassium Iodide, (KI).	Yellowish AgI .	Greenish Hg_2I_2 . Sol. in excess.	Red, HgI_2 . Sol. in excess of either.

Group II—Metals precipitated in acid, or neutral solutions by H_2S , but not in alkaline.

Reagents.	Arsenious.	Arsenic.	Antimonious.	Antimonic.
Hydrogen Sulphide, (H_2S .) (Group reagent.)	Yellow, As_2S_3 . Sol. in alkalis and alkaline sulphides. Insol. in HCl .	Yellow, $As_2S_3 + S_2$, appears slowly, hastened by boiling.	Orange red, Sb_2S_3 . Sol. in HCl , in alkalis and in alkaline sulphides.	Orange, Sb_2S_5 . Sol. in HCl , in alkalis and al- kaline sulphides.
Ammonium Sulphide, (NH_4) $_2S$.	As_2S_3 , only in acid solutions. Sol. in excess.	As_2S_5 , only in acid solutions. Sol. in excess.	Sb_2S_3 . Sol. in ex- cess.	Sb_2S_5 . Sol. in excess.

Group I.—*Continued.*

Lead.	Copper.	Bismuth.	Cadmium.
Yellow PbCrO_4 . Sol. in fixed alkalis. Sparingly sol. in HNO_3 . Insol. in NH_4HO .	Red brown, CuCrO_4 . Sol. in NH_4HO with green color.	Yellow, $\text{Bi}_2(\text{CrO}_4)_3$.	—
White, Pb_2FeCy_6 .	Red brown, Cu_2FeCy_6 . Slightly sol. in NH_4HO .	White precipitate. Bismuth ferrocyanide. Sol. in HCl .	Yellowish white, Cd_2FeCy_6 . Sol. in HCl .
White, PbCl_2 , only in concentrated solutions.	White, Cu_2Cl_2 , only in concentrated solutions. Soluble in HCl .	In the presence of KHO or NaHo , black BiO_2 .	—
Yellow PbI_2 . Soluble in excess upon heating.	White, Cu_2I_2 the liquid contains free Iodine.	Brown, BiI_3 .	White CdI_2 . Only in very concentrated solutions.

Group II.—*Continued.*

Stannous.	Stannic.	Platinum.	Gold.
Brown, SnS . Sol. in HCl , in alkalies, moderately sol. in yellow ammonium sulphide.	Yellow, SnS_2 . Sol. in HCl , in alkalies, in alkaline sulphides, in alkaline carbonates.	Dark brown, PtS_2 . Insol. in HCl . Moderately sol. in alkaline sulphides. Sol. in aqua regia.	Dark, Au_2S_3 . Insol. in HCl . Sol. in alkaline sulphides, in aqua regia.
SnS . Sol. in yellow ammonium sulphide.	SnS_2 . Sol. in excess.	PtS_2 . Sol. in excess.	Au_2S_3 . Sol. in excess.

Group II—Continued.

Reagents.	Arsenious.	Arsenic.	Antimonious.	Antimonic.
Sodium hydroxide, NaHO.	—	—	White, Sb_2O_3 . Sol. in excess. Sol. in HCl and H_2O_2 . Easily reduced by KCN.	White, $NaSbO_3$. Sol. in excess.
Potassium hydroxide, KHO.	—	—	Sb_2O_3 anhydride.	—
Ammonium hydroxide, NH_4HO .	—	—	Sb_2O_3 . Insol. in excess.	NH_4SbO_3 , nearly insol. in excess.
Silver nitrate, $AgNO_3$.	Yellow Ag_3AsO_3 . Sol. in HNO_3 . and in NH_4HO .	Reddish brown, Ag_3AsO_4 . Sol. in HNO_3 , and in NH_4HO .	White precipitate, $AgCl$ and Sb_2O_3 .	White, $AgSbO_3$. Sol. in NH_4HO .
Copper sulphate, $CuSO_4$.	Yellowish green, $Cu_3(AsO_3)_2$. Sol. in HNO_3 , and in NH_4HO , or NaHO.	Greenish blue, $Cu_3(AsO_4)_2$. Sol. in HNO_3 , NH_4HO .	White precipitate. Basic antimonious chloride.	Light brown precipitate. Copper antimoniate
Mercuric chloride, $HgCl_2$.	White, $Hg_3(AsO_3)_2$. Sol. in acids.	—	Basic antimonious chloride.	—
Metallic zinc, Zn.	Arsenic.		Antimony.	
	Generate H_3As —the spots on porcelain are steel gray to black. They dissolve in NaClO. Warmed with $(NH_4)_2S$, forms yellow spots. Soluble in $(NH_4)_2CO_3$, insoluble in HCl. With vapor of iodine, yellow arsenious iodide. Readily volatile when heated.		Generate H_3Sb —the spots on porcelain brown to black. They do not dissolve in NaClO, warmed with $(NH_4)_2S$ forms orange yellow spots, insoluble in $(NH_4)_2CO_3$. Soluble in HCl. With vapor of iodine, carmine red antimonious iodide. Not readily volatile when heated.	

Group II—Continued.

Stannous.	Stannic.	Platinum.	Gold.
White, $\text{Sn}(\text{OH})_2$. Sol. in excess, in HCl . Reduced to metal by KCN —	White, $\text{Sn}(\text{OH})_4$. Sol. in excess.	—	—
$\text{Sn}(\text{OH})_2$. Soluble in excess.	$\text{Sn}(\text{OH})_4$. Soluble in excess.	Yellow, K_2PtCl_6 . Sol. in 12,083 parts absolute alcohol.	—
$\text{Sn}(\text{OH})_2$. Insol. in excess.	$\text{Sn}(\text{OH})_4$. Slightly sol. in excess.	Yellow, $(\text{NH}_4)_2\text{PtCl}_6$. Sol. in 26,535 parts absolute alcohol— sparingly sol. in cold H_2O .	Yellow, $(\text{NH}_3)_2\text{Au}_2\text{O}_3$. In- sol. in excess. [Fulminating gold.]
Silver chloride and metallic silver.	AgCl .	Light brown, $\text{AgCl} + \text{PtO}_2$.	Light brown, $\text{AgCl} + \text{Au}_2\text{O}_3$.
With SnCl_2 , white, Cu_2Cl_2 . Sol. in acids.	—	—	—
SnCl_2 , first white Hg_2Cl_2 —with excess black Hg .	—	—	—
Sn .	Sn and in neutral. Sol. $\text{Sn}(\text{OH})_4$.	Black, Pt .	Brown, Au .

Group III—Metals precipitated by H_2S in alkaline solutions.

Reagents.	Zinc.	Nickel.
Ammonium sulphide, (NH_4) $_2$ S. (Group reagent).	White, ZnS. Insoluble in H, $C_2H_3O_2$, and in KHO.	Black, NiS. Slightly solu- ble in (NH_4) $_2$ S. Nearly insoluble in dilute HCl. Soluble in aqua regia.
Hydrogen sulphide, H_2S .	White, ZnS. In neutral or acetic acid solutions.	Black, NiS in neutral solu- tions.
Sodium hydroxide NaHO.	White, Zn(OH) $_2$. Soluble in excess, reappears on heating.	Apple green, Ni(OH) $_2$. In- soluble in excess. Soluble in NH_4 HO, and (NH_4) $_2$ CO $_3$ with a blue green color.
Ammonium hydroxide, NH_4 HO.	White, Zn(OH) $_2$. Soluble in excess. In presence of NH_4 HO salts no precipitate.	Green, Ni(OH) $_2$. Soluble in excess with blue color. In the presence of NH_4 HO salts no precipitate.
Sodium carbonate, Na $_2$ CO $_3$.	White precipitate, basic salt, Soluble in NaHO and in NH_4 NO.	Apple green, precipitate of basic salt.
Sodium phosphate. Na $_2$ HPO $_4$.	White, Zn $_3$ (PO $_4$) $_2$. Soluble in alkalies. Soluble in KHO and NH_4 HO, also in strong acids.	Light green, Ni $_3$ (PO $_4$) $_2$. Soluble in NH_4 HO.
Barium carbonate, BaCO $_3$.	In the cold, no precipitate if sulphates are absent.	In the cold no precipitate if sulphates are absent.
Potassium ferrocyanide, K $_4$ FeCy $_6$.	White, Zn $_2$ FeCy $_6$. Soluble in HCl.	Greenish white, Ni $_2$ FeCy $_6$. Insoluble in HCl.
Potassium ferricyanide, K $_3$ FeCy $_6$.	Brownish yellow, Zn $_3$ (FeCy) $_2$. Soluble in HCl and NH_4 HO.	Yellowish green, Ni $_3$ (FeCy $_6$) $_2$. Insoluble in HCl.

Group III—Continued.

Cobalt.	Iron. (<i>ous</i>)	Manganese.
Black, CoS. Insoluble in excess. Insoluble in $\text{HC}_2\text{H}_3\text{O}_2$. Nearly insol. in HCl. Sol. in aqua regia.	Black, FeS. Sol. in HCl and $\text{HC}_2\text{H}_3\text{O}_2$. In the air oxidizes.	Flesh colored, MnS. Soluble in HCl and $\text{HC}_2\text{H}_3\text{O}_2$. In the air, oxidizes.
Black, CoS in neutral solutions.	—	—
Blue, hydroxide or basic salts. Insoluble in excess. Soluble in NH_4HO and in $(\text{NH}_4)_2\text{CO}_3$ with violet color.	White, $\text{Fe}(\text{OH})_2$, soon oxidizes to green and brown red. Insoluble in excess.	White, $\text{Mn}(\text{OH})_2$, soon oxidizes to brown, Mn_2O_3 . Insoluble in excess
Blue, hydroxide or basic salts. Soluble in excess with brownish red color.	White, $\text{Fe}(\text{OH})_2$ becomes green and brown. Incomplete precipitation.	White, $\text{Mn}(\text{OH})_2$. In the presence of NH_4Cl not precipitated. On standing becomes brown. Mn_2O_3 and precipitates.
Peach red, basic salts. On heating becomes violet and blue.	White, basic salts, becomes brown in the air. Soluble in NH_4HO salts.	White, MnCO_3 . Somewhat soluble in NH_4HO salts.
Light red, $\text{Co}_3(\text{PO}_4)_2$. Soluble in NH_4HO .	White, $\text{Fe}_3(\text{PO}_4)_2$. Soluble in NH_4HO . In the air becomes blue or green.	White, $\text{Mn}_3(\text{PO}_4)_2$. Soluble in NH_4HO salts.
In the cold, no precipitate, if sulphates are absent.	In the cold no precipitate. See (<i>ic</i>) iron.	In the cold, no precipitate, if sulphates are absent.
Green, Co_2FeCy_6 becomes dark. Insoluble in HCl.	White, $\text{Fe}_2\text{FeCy}_6 + \times \text{K}_4\text{FeCy}_6$ becomes blue. Insoluble in HCl. NaHO separates $\text{Fe}(\text{OH})_2$.	Whitish red, Mn_2FeCy_6 . Soluble in HCl.
Dark brown, $\text{Co}_3(\text{FeCy}_6)_2$. Insoluble in HCl.	Dark blue, $(\text{Fe}_3\text{FeCy}_6)_2$. Insoluble in HCl, NaHO decomposes it.	Brown, $\text{Mn}_3(\text{FeCy}_6)_2$. Soluble in HCl.

Group III—(Section containing sesquioxides.)—*Continued.*

Reagents.	Aluminum.	Iron. (<i>ic</i>)	Chromium.	Uranium.
Ammonium sulphide, $(\text{NH}_4)_2\text{S}$. (Group reagent.)	White, $\text{Al}_2(\text{OH})_6$.	Black, $\text{FeS} + \text{S}$. Soluble in acids forming a ferrous salt.	Greenish gray, $\text{Cr}_2(\text{OH})_6$.	Brownish black, UO_2S . Moderately soluble in $(\text{NH}_4)_2\text{S}$. Insol. in presence of $(\text{NH}_4)_2\text{CO}_3$.
Barium carbonate, BaCO_3 .	White, $\text{Al}_2(\text{OH})_6$.	Light brown, basic salts.	Greenish basic salt.	Yellow, $\text{UO}_2(\text{OH})_2$.
Sodium phosphate, Na_2HPO_4 .	White, AlPO_4 . Sol. in alkalis and reprecipitated by NH_4Cl .	White, FePO_4 . Sol. in excess. Insoluble in $\text{HC}_2\text{H}_3\text{O}_2$.	Green, CrPO_4 .	Yellowish white, UO_2HPO_4 . Sol. in excess, also in NH_4HO . In $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2$ but not in $\text{HC}_2\text{H}_3\text{O}_2$.
Potassium ferrocyanide, K_4FeCy_6 .	—	Prussian blue, $\text{Fe}_4(\text{FeCy}_6)_3$. Insol. in HCl . NaHO precipitates $\text{Fe}_2(\text{OH})_6$.	—	Red brown, $\text{K}_4\text{FeCy}_6 + 2\text{UO}_2\text{FeCy}_6$.
Potassium sulphocyanate, KCNS .	—	Blood red, $\text{Fe}(\text{CNS})_3$. Solution.	—	Red solution.
Ammonium hydroxide, NH_4HO .	White, $\text{Al}_2(\text{OH})_6$. Slightly soluble in excess.	Brown red, $\text{Fe}_2(\text{OH})_6$.	Greenish blue, $\text{Cr}_2(\text{OH})_6$. Slightly soluble in excess with violet color, precipitated on boiling.	Yellow, $(\text{NH}_4)_2\text{U}_2\text{O}_7$.

Group III—Continued.

Reagents.	Aluminium.	Iron, (<i>ic</i>)	Chromium.	Uranium.
Ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$.	White, $\text{Al}_2(\text{OH})_6$.	Brown red, basic carbonate.	Grayish green, $\text{Cr}_2(\text{OH})_6$. Sol. in excess.	Yellow, $2(\text{NH}_4)_2\text{CO}_3 + (\text{UO})_2\text{CO}_3$. Sol. in excess. Precipitated by fixed alkalies
Sodium hydroxide, (NaHO) .	White, $\text{Al}_2(\text{OH})_6$. Sol. in excess. On heating with NH_4Cl reprecipitated.	Brownish red, $\text{Fe}_2(\text{OH})_6$. Insol. in excess.	Bluish green, $\text{Cr}_2(\text{OH})_6$. Sol. in excess— with green color, on heating reprecipitates.	Yellow, $\text{Na}_2\text{U}_2\text{O}_7$. Sol. in $(\text{NH}_4)_2\text{CO}_3$.

Group IV—Metals precipitated by $(\text{NH}_4)_2\text{CO}_3$ but not by H_2S .

Reagents.	Magnesium.	Barium.	Strontium.	Calcium.
Sodium phosphate, $(\text{Na}_2\text{HPO}_4)$.	White, MgHPO_4 , only in concentrated solution. In presence of NH_4HO and in dilute solution $\text{Mg}(\text{NH}_4)\text{PO}_4$.	White, BaHPO_4 . Sol. in acids— reprecipitated by NH_4HO .	White, SrHPO_4 . Sol. in acids, reprecipitated by NH_4HO .	White, CaHPO_4 . Sol. in acids, reprecipitated by NH_4HO .
Flame.	—	Yellowish green.	Carmine.	Yellowish red.

Group IV—Continued.

Reagents.	Magnesium.	Barium.	Strontium.	Calcium.
Ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$. (Group reagent.)	White, $\text{MgCO}_3 + \times \text{Mg}(\text{OH})_2$. Sol. in 10,000 parts H_2O . Sol. in ammonium salts	White, BaCO_3 . Sol. in 14,137 parts H_2O . Sol. in HNO_3 and HCl .	White, SrCO_3 . Sol. in 18,045 parts of H_2O . Sol. in 56,545 parts of H_2O , containing NH_4HO .	White, CaCO_3 . Sol. in 10,601 parts cold H_2O . Sol. in HNO_3 , and HCl . H_2O containing NH_4HO , requires 63,246 parts to dissolve it.
Sodium hydroxide, (NaHO) .	White, $\text{Mg}(\text{OH})_2$. Sol. in ammonium salts.	White, $\text{Ba}(\text{OH})_2$, only in concentrated solutions.	White, $\text{Sr}(\text{OH})_2$, difficultly sol. in H_2O .	White, $\text{Ca}(\text{OH})_2$, difficultly sol. in H_2O .
Ammonium hydroxide, (NH_4HO) .	White, $\text{Mg}(\text{OH})_2$. Sol. in ammonium salts.	—	—	—
Sulphuric acid, (H_2SO_4) or a soluble sulphate.	—	White, BaSO_4 . Sol. in 200,000 parts H_2O . Sparingly sol. in acids.	White, SrSO_4 . Sol. in 6,895 parts H_2O .	White, CaSO_4 . Sol. in 500 parts H_2O . Insol. in alcohol.
Ammonium oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4$	—	White, BaC_2O_4 . Sol. in 2,590 parts H_2O . Sol. in $\text{HC}_2\text{H}_3\text{O}_2$. Quite sol. in dilute $\text{H}_2\text{C}_2\text{O}_4$.	White, SrC_2O_4 . Sol. in 12,000 parts H_2O . Slightly sol. in $\text{H}_2\text{C}_2\text{O}_4$. Slightly sol. in NH_4 salts.	White, CaC_2O_4 . Sol. in 500,000 parts H_2O . Insol. in $\text{H}_2\text{C}_2\text{O}_4$, or $\text{HC}_2\text{H}_3\text{O}_2$.
Potassium chromate, (K_2CrO_4) .	—	Yellow, BaCrO_4 . Difficultly sol.	Yellow, SrCrO_4 . Moderately sol. in H_2O .	Whitish, CaCrO_4 . Easily soluble.
Hydrofluosilicic acid, (H_2SiF_6) .	—	White, BaSiF_6 . Sparingly sol. in H_2O .	—	White, CaSiF_6 . Easily soluble.

Group V—Metals not precipitated by H_2S nor by $(\text{NH}_4)_2\text{CO}_3$.

Reagents.	Potassium.	Ammonium.	Lithium.	Sodium.
Sodium carbonate, (Na_2CO_3) .	—	—	White, Li_2CO_3 . Slightly sol. in H_2O .	—
Sodium Phosphate, $(\text{Na}_2\text{HPO}_4)$.	—	—	White, Li_3PO_4 . Sol. in 2,539 parts of H_2O . Sol. in 3,920 parts of dilute ammonia.	—
Platinic chloride, (PtCl_4) .	Yellow, K_2PtCl_6 . Sol. in 12,083 parts of absolute alcohol. Slightly sol. in H_2O .	Yellow, $(\text{NH}_4)_2\text{PtCl}_6$. Sol. in 26,535 parts of absolute alcohol.	—	—
Tartaric acid $(\text{H}_2\text{C}_4\text{H}_4\text{O}_6)$.	White crystal, $\text{KHC}_4\text{H}_4\text{O}_6$, forms better after shaking. Sparingly sol. in H_2O . Sol. in HCl and in alkalies.	White crystal, $\text{NH}_4\text{HC}_4\text{H}_4\text{O}_6$. Slightly sol. in H_2O . Sol. in alkaline solutions, and the mineral acids.	—	—
Potassium antimoniate, $(\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7)$.	—	—	—	White crystal, $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$. Insol. in alcohol. Sparingly sol. in H_2O . Sol. in alkaline solutions
Nessler's reagent, sol. of HgI_2 in $\text{KI} + \text{KHO}$.	—	Yellowish brown, NHg_2I .	—	—
Hydrofluosilicic acid, (H_2SiF_6) .	Translucent, K_2SiF_6 . Insol. in alcohol. Sol. in 790 parts H_2O . Sol. in HCl .	—	—	White, Na_2SiF_6 . Difficultly sol. in H_2O .
Flame reaction.	Violet.	—	Red.	Yellow.

Reactions of the acids.

Soluble Salts of the following Acids.	Barium Chloride.	Calcium Chloride.	Silver Nitrate.
Sulphuric acid, H_2SO_4 .	White, BaSO_4 . Insol. in acids.	White, CaSO_4 . Sol. in 480 parts H_2O . in 3 parts HCl .	White, Ag_2SO_4 , only in concentrated sol.
Sulphurous acid, H_2SO_3 .	White, BaSO_3 . Sol. in HCl .	White, CaSO_3 . Sol. in HCl .	White, breaks up by heating into Ag_2 , Ag_2SO_4 and SO_2 .
Thiosulphuric acid, $\text{H}_2\text{S}_2\text{O}_3$.	White, BaS_2O_3 , only in concentrated sol.	—	White precipitate. Sol. in $\text{Na}_2\text{S}_2\text{O}_3$, quickly breaks up & yields black Ag_2S .
Ortho Phosphoric acid, H_3PO_4 .	White, $\text{Ba}_3(\text{PO}_4)_2$. Sol. in acids also in NH_4Cl .	White, $\text{Ca}_3(\text{PO}_4)_2$. Sol. in acids, and in NH_4Cl .	Yellow, Ag_3PO_4 . Sol. in HNO_3 . Sol. in NH_4HO .
Pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$.	White, $\text{Ba}_2\text{P}_2\text{O}_7$. Sol. in HCl .	White, $\text{Ca}_2\text{P}_2\text{O}_7$. Soluble in excess,	White, $\text{Ag}_4\text{P}_2\text{O}_7$. Sol. in HNO_3 . Sol. in NH_4HO .
Metaphosphoric acid, HPO_3 .	White, $\text{Ba}(\text{PO}_3)_2$. Sol. in excess of HPO_3 .	White, $\text{Ca}(\text{PO}_3)_2$.	White, AgPO_3 . Sol. in HNO_3 . Sol. in NH_4HO .
Arsenic acid, H_3AsO_4 .	White, $\text{Ba}_3(\text{AsO}_4)_2$. Sol. in NH_4Cl . Sol. in acids.	White, $\text{Ca}_3(\text{AsO}_4)_2$. Sol. in NH_4Cl . Sol. in acids.	Red brown, Ag_3AsO_4 . Sol. in HNO_3 . Sol. in NH_4HO .
Arsenious acid, H_3AsO_3 .	White, $\text{Ba}_3(\text{AsO}_3)_2$. Sol. in NH_4Cl . Sol. in acids.	White, $\text{Ca}_3(\text{AsO}_3)_2$. Sol. in NH_4Cl . Sol. in acids.	Light Yellow, Ag_3AsO_3 . Sol. in HNO_3 . Sol. in NH_4HO .
Chromic acid, H_2CrO_4 .	Yellow, BaCrO_4 . Sol. in HCl and HNO_3 . Insol. in $\text{HC}_2\text{H}_3\text{O}_2$.	Light yellow, CaCrO_4 . Only in neutral so- lutions and easily sol. in H_2O .	Dark red, Ag_2CrO_4 . Sol. in HNO_3 .
Boric acid, H_3BO_3 .	White, $\text{Ba}_3(\text{BO}_3)_2$. Sol. in acids. Sol. in NH_4Cl .	White, $\text{Ca}_3(\text{BO}_3)_2$. Sol. in acids. Sol. in NH_4Cl and in CaCl_2 .	White, Ag_3BO_3 . Sol. in HNO_3 . Sol. in NH_4HO .
Phosphorous acid, H_3PO_3 .	White, $\text{Ba}_3(\text{PO}_3)_2$. Sol. in $\text{HC}_2\text{H}_3\text{O}_2$.	White, $\text{Ca}_3(\text{PO}_3)_2$. Sol. in NH_4Cl .	White, Ag_3PO_3 . Black metallic Ag when heated.
Silicic acid, H_4SiO_4 .	White, Ba_2SiO_4 .	White, Ca_2SiO_4 .	Yellow Ag_4SiO_4 in concentrated solu- tions. Sol. in HNO_3 and in NH_4HO .
Carbonic acid, H_2CO_3 .	White, BaCO_3 . Sol. in acids.	White, CaCO_3 . Sol. in acids.	White, Ag_2CO_3 . Sol. in HNO_3 .
Nitric acid, HNO_3 .	—	—	—
Chloric acid, HClO_3 .	—	—	—
Iodic acid, HIO_3 .	White, $\text{Ca}(\text{IO}_3)_2$ dif- ficultly soluble. Sol. in HNO_3 .	—	White, AgIO_3 . Sol. in NH_4HO . Treated with SO_2 is reduced to AgI .
Hydrofluoric acid, HF .	White, bulky BaF_2 . Sol. in HCl in HNO_3 . in NH_4Cl .	White gelatinous CaF_2 . Sol. in HCl and in NH_4Cl . Insol. in $\text{HC}_2\text{H}_3\text{O}_2$.	—
Hydrofluosilicic acid H_2SiF_6 .	White, BaSiF_6 . In- sol. in HCl & in HNO_3 .	White, CaSiF_6 . Sol. in HCl .	—

Reactions of the acids—*Continued.*

Lead Acetate.	Special Reactions.
White, PbSO_4 . Sol. in KHO , and $(\text{NH}_4)\text{HC}_4\text{H}_4\text{O}_6$.	S, Se, Te, give when heated with Mg in a thin glass tube—or when heated with Na_2CO_3 on charcoal, a hepar. Sulphide reaction is shown best on silver coin.
White, PbSO_3 .	Reduces, KMnO_4 , starch iodide and other bodies—good reducing agent, gives a hepar.
White, PbS_2O_3 . When heated gray= $\text{PbS} + \text{PbSO}_4$.	Breaks up with HCl into SO_2 , S and H_2O , gives a hepar. $\text{Na}_2\text{S}_2\text{O}_3$, dissolves AgCl , AgI , HgCl , PbSO_4 .
White, $\text{Pb}_3(\text{PO}_4)_2$. Sol. in KHO . Insol. in NH_4HO .	$(\text{NH}_4)_2\text{MoO}_4$ in HNO_3 gives a yellow ammonium phosphomolybdate of variable composition. $\text{MgCl}_2 + \text{NH}_4\text{Cl} + \text{NH}_4\text{HO}$ gives white $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$.
White gelatinous $\text{Pb}_2\text{P}_2\text{O}_7$. Sol. in excess of $\text{H}_4\text{P}_2\text{O}_7$.	Does not coagulate albumin. No precipitate with BaCl_2 .
White, $\text{Pb}(\text{PO}_3)_2$. Insol. in excess. Sol. in HNO_3 .	Coagulates albumin—gives white precipitate with CaCl_2 and with BaCl_2 .
White, $\text{Pb}_3(\text{AsO}_4)_2$. Sol. in HNO_3 . Insol. in $\text{HC}_2\text{H}_3\text{O}_2$.	Gives yellow a precipitate with ammonium molybdate. White with magnesia mixture.
White, $\text{Pb}_3(\text{AsO}_3)_2$. Sol. in $\text{HC}_2\text{H}_3\text{O}_2$.	In Marsh's apparatus As spots—see page 160
Yellow, PbCrO_4 . Soluble in KHO .	$\text{H}_2\text{O}_2 + \text{C}_4\text{H}_{10}\text{O}$ give with CrO_3 a fine blue color. SnCl_2 reduces it to a green colored solution of Cr_2O_3 .
White, $(\text{Pb})_3(\text{BO}_3)_2$. Sol. in excess of Pb salt.	HCl and H_2SO_4 decompose strong solutions of borates. Free B_2O_3 colors non luminous flame, green. [Add H_2SO_4 or glycerin to borax bead.]
White, $\text{Pb}_3(\text{PO}_3)_2$. Insoluble in $\text{HC}_2\text{H}_3\text{O}_2$.	Reducing agent. When it is rapidly boiled H_3P is evolved.
White precipitate, Soluble in HNO_3 .	Gives with salt of phosphorus a skeleton bead—with HF the silicate SiF_4 forms.
White, PbCO_3 . Sol. in HNO_3 . Soluble in 50,551 parts H_2O .	The stronger acids liberate CO_2 —which if passed into lime water renders it turbid.
—	Add H_2SO_4 and cool it, then a crystal of FeSO_4 —yields a dark brown ring. Brucin dissolved in H_2SO_4 , gives red color, very delicate test.
—	When heated on charcoal deflagrates. Free O can be tested by ignited splinter.
White, $\text{Pb}(\text{IO}_3)_2$.	Add KI , now treat with $\text{HC}_2\text{H}_3\text{O}_2$, I is liberated, known by brown color, dissolve with CS_2 —gives red color
White, PbF_2 . Soluble in HNO_3 .	H_2SO_4 liberates HF gas, which etches glass.
—	K salts difficultly soluble. With H_2SO_4 : HF , and SiF_4 are liberated,

Reactions of the acids—*Continued.*

Soluble Salts of the following Acids.	Barium Chloride.	Calcium Chloride.	Silver Nitrate.
Hydrochloric acid, HCl.	—	—	White, AgCl. Sol. in NH_4HO , in KCN, in $\text{Na}_2\text{S}_2\text{O}_3$.
Hydrobromic acid, HBr.	—	—	Yellowish, AgBr. Dif. sol. in NH_4HO .
Hydriodic acid, HI.	—	—	Yellowish white, AgI. Blackens in the light. Spar. sol. in NH_4HO .
Hydrocyanic acid, HCN.	—	—	White, AgCN. Sol. in NH_4HO , & in KCN. Insol. in dilute acids. When ignited yields metallic silver.
Hydrosulphocyanic acid, HCNS.	—	—	White, AgCNS. Sol. in NH_4HO & in KCN. Insol. in dilute HNO_3 . Blackens in the light.
Hydrosulphuric acid, H_2S .	—	—	Black, Ag_2S . [See page 156.]

Organic acids.

Soluble Salts of the following acids.	Calcium Chloride.	Silver Nitrate.
Formic acid, HCHO_2 .	—	White, then black. The silver is reduced.
Acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$.	—	White, $\text{AgC}_2\text{H}_3\text{O}_2$ only in concentrated solutions. Sol. in hot water. When ignited becomes white Ag.
Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$.	White, CaC_2O_4 . Insoluble in $\text{HC}_2\text{H}_3\text{O}_2$, and in NH_4Cl .	White, $\text{Ag}_2\text{C}_2\text{O}_4$. Sol. in HNO_3 . Decomposes when heated above 116°C .
Tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$.	White, $\text{CaC}_4\text{H}_4\text{O}_6$. Sol. in NH_4Cl & KHO . On heating the alk. salt precipitates & again dissolves on cooling.	White, $\text{Ag}_2\text{C}_4\text{H}_4\text{O}_6$ (not in free $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$). Sol. in NH_4HO . Boiling this solution precipitates Ag.
Malic acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_5$.	White precipitate, only in the presence of strong alcohol.	White precipitate.
Citric acid, $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$.	White, $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2$ (not in the free acid). Sol. in NH_4Cl . Insol. in KHO . Less sol. in warm than cold water.	White precipitate

	Ferric Chloride.	Silver Nitrate.
Succinic acid, $\text{C}_4\text{H}_6\text{O}_4$.	Its alkaline salts give a light yellow precipitate.	White precipitate.
Benzoic acid, $\text{C}_7\text{H}_6\text{O}_2$.	Flesh color. Soluble in HCl.	White precipitate. Soluble in hot water.
Salicylic acid, $\text{C}_7\text{H}_6\text{O}_3$.	Deep violet color.	White precipitate. Soluble in hot water.
Gallic acid, $\text{C}_7\text{H}_6\text{O}_5$.	Bluish black precipitate.	Reduced to metallic Ag.
Tannic acid, $\text{C}_{14}\text{H}_{10}\text{O}_9$.	Bluish black color.	White precipitate.

Reactions of the acids—*Continued.*

Lead Acetate.	Special Reactions.
White, PbCl_2 . Soluble in 30 parts hot water.	With $\text{H}_2\text{SO}_4 + \text{MnO}_2$ Cl_2 is given off. With CrO_3 , red CrO_2Cl_2 is given off.
White, PbBr_2 . Soluble in hot water.	When liberated by Cl and treated with CS_2 or $\text{C}_4\text{H}_{10}\text{O}$, gives a red color.
Yellow, PbI_2 . Soluble in hot water, on cooling yields golden colored crystals.	When treated with strong HNO_3 , I is set free, and gives with CS_2 or better CHCl_3 violet color, in stronger solutions blue.
White, $\text{Pb}(\text{CN})_2$. Soluble in HNO_3 . Insoluble in KCN .	When treated with $(\text{NH}_4)_2\text{S}$ and gently evaporated to dryness forms with ferric salts a blood red color. Warmed with $\text{KHO} + \text{FeSO}_4$ and a little FeCl_6 , and then acidulated with HCl , forms Prussian blue.
White, $\text{Pb}(\text{CNS})_2$.	With FeCl_6 blood red color, add HgCl_2 the color vanishes,
Black, PbS . See page 3.	In alkaline solution with nitroprusside of sodium violet color—very delicate reaction.

Organic acids—*Continued.*

Lead Acetate.	Special Reactions.
—	Reducing agent. With concentrated H_2SO_4 , CO_2 is given off.
—	With FeCl_6 , red brown solution, on heating precipitates. On heating with $\text{C}_2\text{H}_6\text{O} + \text{H}_2\text{SO}_4$ forms acetic ether. On heating with As_2O_3 forms cacodyl.
White, PbC_2O_4 . Sol. in HNO_3 , Insol. in $\text{HC}_2\text{H}_3\text{O}_2$.	The acid K and NH_4 salts difficultly soluble.
White, $\text{PbC}_4\text{H}_4\text{O}_6$. Sol. in HNO_3 . Slightly sol. in NH_4Cl . Insol. in alcohol.	With $\text{MnO}_2 + \text{H}_2\text{SO}_4$ heated, CO_2 is given off. When heated on Pt foil gives odor of burned sugar.
White, $\text{PbC}_4\text{H}_4\text{O}_5$. Melts on heating.	Add $\text{CaCl}_2 + \text{C}_2\text{H}_6\text{O}$ white $\text{CaC}_4\text{H}_4\text{O}_5$ even in dilute neutral solutions. Sol. in water. Insol. in alcohol.
White, $\text{PbHC}_6\text{H}_5\text{O}_7$. Sol. in HNO_3 , and in ammonium citrate.	Melts when heated, and at 175°C . gives off pungent, characteristic vapors, containing acetone. It prevents the precipitation of iron and the other heavy metals by the alkalis. Solution of lime gives no precipitate in the cold, (while Tartaric, Racemic and Oxalic acids do.)

Lead Acetate.	Special Reactions.
White, $\text{PbC}_4\text{H}_4\text{O}_4$. Sol. in excess of either. Sol. in HNO_3	Melts at 180°C . With FeCl_6 , a brownish red bulky precipitate of basic ferric succinate—quantitative method of estimation.
Its alkaline salts give a white precipitate.	Melts at 120°C . Sublimes. Where heated in a test tube with HNO_3 nitrobenzole is evolved, odor of bitter almond oil.
White precipitate.	Melts at 155°C . Its vapors causes irritation in the throat, and has a sweetish sour taste. When heated with methylic alcohol and concentrated sulphuric acid, salicylate of methyl is evolved, having the odor of winter green.
—	Melts at 200°C . The alkaline solution absorbs oxygen, with $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ brown to black precipitate.
Yellowish precipitate.	With molybdate of ammonia a red color, removed by oxalic acid, precipitates gelatin and albumin, (distinctions from gallic acid). Has an astringent taste.

FACTS, HYPOTHESES, AND LAWS EMPLOYED IN CHEMISTRY.

I. RELATING TO GASES ONLY.

Charles (1787). The volume of a gas is directly proportioned to its absolute temperature— $T - 273^{\circ} \text{C}$.

Mariotte or Boyle (1662). The volume of a gas is inversely proportioned to its external pressure. The elastic force of a gas exactly corresponds to its external pressure. The density of a gas is directly proportioned to its external pressure.

The volume and density of a gas vary both with temperature and pressure.

Graham (1832). The rate of diffusion of gases is inversely proportioned to the square root of their density.

Avogadro (1811). Equal volumes of different gases contain the same number of molecules.

Gay Lussac (1805). Two gases combine by simple volumetric ratios; as, HH , HCl , $\text{H}_2\text{O} - \text{H}_3\text{N}$, H_4C , condensing in all cases to two volumes. The vapor density of a gas is half its molecular weight.

Deville (1857). Overheated compound gases become dissociated; as, NH_3 , HCl , the vapor density becoming the mean of the molecular weights.

Meyer (1842). Even elementary molecules may dissociate; as, I_2 . Compare vapor density of S at different temperatures.

Clausius and Maxwell (1867). The elastic force of a gas may be expressed in terms of a "dynamical theory," in which the factors are the number of gaseous molecules (N), their mass (M), their rate of motion (V). The elastic force, $\frac{1}{3} MNV^2$.

By general agreement, hydrogen is taken as the standard unit:

- I. For density or specific gravity of gases—relative weight of equal volumes.
- II. For molecular volume—its volume in the free state; 11.2 liters weigh gram.
- III. For atomic weight, H being 1, $\text{O} = 15.9633$; O being 16, $\text{H} = 1.0023$.
- IV. For combining power—chlorine, potassium, and other elements being reckoned its equivalent.

II. RELATING TO ALL ELEMENTS.

Dalton (1804). Elements combine in definite and invariable proportions by weight, H being 1, $\text{Cl} = 35.5$, $\text{K} = 39.1$, etc.

These proportions may, and do increase by multiples; as, N_2O , NO , N_2O_3 , N_2O_4 , or NO_2 , N_2O_5 .

The simplest rational combining proportion of an element is its *Atomic Weight*, in H_2O , $\text{O} = 16$; in H_3N , $\text{N} = 14$.

Wollaston (1809). The least combining proportion of an element is its equivalent: in H_2O , $\text{O} = 8$; in H_3N , $\text{N} = 4.6$.

The densities of gaseous elements determine their atomic weight (H being 1).

Accurate analyses of well defined compounds and assisted by comparison of analogous compounds, are required for ascertaining the atomic weight of the other elements. Assisting in this determination, or confirming the weight assigned, are:

Dulong and Petits (1819). The atomic heats of all elements is the same (sp. heat \times at. wt. = 6.4, nearly).

Kopp's. Compounds analogously constituted have the same molecular heat.

Mitscherlich's (1819). Solid compounds analogously constituted have the same crystalline form; *i. e.*, are isomorphous, K_2O with Na_2O , FeO with MgO , Fe_2O_3 with Al_2O_3 .

Prout's Hypothesis (1815). Maintains that the atomic weights may be expressed in whole numbers (nearly true for about 39).

III. THE STRUCTURE OF COMPOUNDS.

Berzelius (1818). All elements may be arranged in an electro chemical series ($+$ positive, $-$ negative), from caesium to oxygen.

Compounds are dual, containing $+$ and $-$ constituents; as oxygen ternary compounds basic and acid $\overset{+}{K_2O} \overset{-}{SO_2}$.

Compound radicals exist which are units like the atoms of elements; as, $K(CN)$, $NH_2(H)$.

Gerhardt and Laurent (1837). All compounds may be arranged in groups after types, HH , HCl , H_2O , H_3N , H_4C —taken once or more than once.

Kekule (1858). Elements have a combining power or valency—odd perissads, even artiaads, from 1 to 8, $\overset{I}{H}$, $\overset{II}{O}$, $\overset{III}{N}$, $\overset{IV}{C}$, $\overset{V}{P}$, $\overset{VI}{S}$, $\overset{VII}{Cl}$, $\overset{VIII}{Os}$.

Compound radicals have also combining power— $\overset{I}{(HO)}$, $\overset{II}{(CO)}$, $\overset{III}{(PO)}$.

Polyvalent elements and radicals may partially saturate each other, forming condensed nuclei or radicals. The opened and closed chain.

The lower hydrocarbons are generally in open or cleft chains.

The aromatic hydrocarbons start from a closed chain.

Mendelejeff (1870). In accordance with these facts and accepted theories, all the elements may be arranged in groups and series, thereby forming "*periods*," in each of which several elements exhibit gradational properties—physical, chemical, and physiological.

IV. FORMATION OF COMPOUNDS.

Compounds are formed by direct union of their constituents. by substitution. and by double exchange.

Bertholett's (1801). Solids separate from mixed solutions by reason of the less solubility of a compound formed by exchange. Gases volatilize from heated mixtures, which give rise to compounds of easy volatility.

Bunsen's (1860). The relative mass of the bodies present in a mixture has a controlling influence on the result.

It takes time to effect most chemical changes—varying from almost instantaneous explosions to very slow crystallization.

In ordinary chemical work, many successive littles are better than one large addition of a reagent.

Heat hastens the solution, and retards the precipitation of most of the elements.

CHAPTER VI.

EXAMINATION OF WATER.

The results of water analyses are reported in parts per 1,000,000, parts per 100,000, and grains per gallon.

The English gallon* of water weighs 70,000 grains, and 70 cubic centimeters of water weigh 70,000 milligrams; so 70 cubic centimeters (C. c.) of water is a *miniature* gallon where milligrams correspond to grains.

Total solids. Seventy C. c. of the water is taken and evaporated, in a platinum dish, on the water bath to *dryness*; the increased weight is the *total* solids. Separate portions of this residue are taken for the determination of CO_2 , H_2SO_4 , etc. Another and larger portion is taken for the determination of the bases.

286. Chlorine is usually in combination with sodium as NaCl . An excess (pure water contains hardly any) commonly indicates contamination with sewage. Chlorine is determined by nitrate of silver: $\text{AgNO}_3 + \text{NaCl} = \text{AgCl} + \text{NaNO}_3$. The molecular weight of AgNO_3 is 170, and the atomic weight of Cl is 35.5; 170 parts of AgNO_3 precipitate 35.5 parts of chlorine, or 4.79 parts of $\text{AgNO}_3 = 1$ part of Cl . Dissolve 4.79 grams of AgNO_3 in one liter of distilled water; one C. c. of this solution will precipitate one milligram of chlorine. The operation is conducted as follows: Seventy C. c. of the water is placed in a *clean* and *white* porcelain dish, or in a broad beaker that rests upon a

* An English gallon is equal to about 1.2 American gallons.

sheet of white paper. Three C. c. of a *neutral* solution* of pure chromate of potash are added and well mixed. The beaker can be one-half filled with distilled water, in order to make it more dilute, when the change from the *white* AgCl to the *red* Ag_2CrO_4 is more easily seen. AgNO_3 is run in from a burette, with constant stirring, until the color becomes permanently tinged with red. The number of C. c. used indicates grains of Cl to the gallon. If the water to be examined is *acid*, it must be neutralized with Na_2CO_3 . An acid condition of the water may dissolve the Ag_2CrO_4 . If the amount of chlorine is *small*, the water can be boiled down one-half or one-fourth its volume before being tested. If the amount of chlorine is large, it can be diluted with three or four times its volume of distilled water. It is a good plan to have the same quantity of distilled water in a beaker of the same size with the same amount of K_2CrO_4 , so as to compare the first tinge of *red* Ag_2CrO_4 that forms. *In every case of doubt make a blank trial with distilled water, or with water containing a known quantity of chlorine.*† This remark will apply to *all* the elements tested in water analysis. A little calculation will enable the student to use any solution that he has made of silver or other reagent; but if he has to make them, the solutions described will save him some calculation.

287. Hardness. Ten grams of good castile soap are dissolved in a liter of thirty-five per cent. alcohol, when one C. c. will precipitate one milligram of carbonate of lime. This must be verified by testing it with 1.11 grams fused CaCl_2 dissolved in one liter of water, when one C. c. = one milligram of CaCO_3 (CaCO_3 molecular weight = 100, while molecular weight of CaCl_2 is 111). The soap solution, if not correct, can be made stronger or weaker until it is correct in strength, or its value can be found and the factor used. Seventy C. c. of water is taken. This is

* Fifty grams of K_2CrO_4 , diluted to a liter; AgNO_3 is added to a *permanent red* to precipitate any accidental chlorine in the salt; filter, and use the filtrate.

† Dissolve 1.65 grams of *pure* NaCl in a liter of distilled water. One C. c. contains one milligram of chlorine. It is found as follows: $\frac{\text{NaCl}}{\text{Cl}} = 1.65$.

diluted with three or four times as much distilled water, and 70 C. c. of the mixture is used as a test. The soap solution is run in, with constant shaking, until the lather lasts five minutes when the vessel is placed upon the side. The number of C. c. of soap solution used gives the degrees of hardness. An example will illustrate it. Seventy C. c. of the water was diluted with 210 C. c. of distilled water. Seventy C. c. of this mixture required ten C. c. of soap solution, the whole would require forty C. c. of the soap solution; but seventy C. c. of *distilled* water requires one C. c. of soap solution, therefore the water required $40 - 3 = 37$ degrees of hardness. When this hardness is occasioned by the presence of calcium and magnesium as soluble bicarbonates, boiling the water converts them into insoluble carbonates, which precipitate, and the water becomes soft. This hardness is called *temporary*, while *permanent* hardness, being caused by the presence of sulphates, is not remedied by boiling. The *total* hardness is determined before boiling, the *permanent* hardness after boiling; the *temporary* hardness is the difference between the two. Lime and magnesia solutions act very differently towards soap solution. Lime forms immediately; magnesia, more slowly, and requires one and one-half times (75 is to 42) as much soap as lime. The lime can be precipitated with oxalate of ammonia, and the filtrate tested for the hardness due to magnesia.

288. Organic matter. The following solutions will be required:

1. *Nessler's reagent* is made by taking thirty-five grams of KI, thirteen grams of HgCl_2 , and 800 C. c. of water. The materials are heated to boiling, and the salts dissolve; to this is added a cold saturated solution of HgCl_2 in water until the red precipitate just begins to be permanent; to this is added 168 grams of KHO or 120 grams of NaHO, whichever is most convenient, and the whole made up to a liter with distilled water. It is allowed to settle, and then put away in a large bottle, well corked. The solution is poured into a small bottle, as required for use; two cubic centimeters are used for a test.

2. *Permanganate solution* is made by dissolving eight grams of $K_2Mn_2O_8$ and 200 grams of KHO in a liter of water. Use fifty C. c. for each analysis. *Always examine the permanganate solution for ammonia* by distilling the solution and adding as much distilled water, free from ammonia, as has been distilled off. In case you can not free it from ammonia, distill it until the amount of ammonia becomes *constant*, and *subtract* this from the ammonia found in the water.

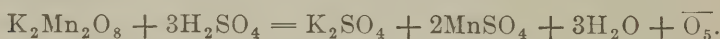
3. *Standard solution of ammonia*—Dissolve 3.15 grams of NH_4Cl in a liter of distilled water. Each C. c. contains one milligram of ammonia, $\frac{NH_4Cl}{NH_3} = \frac{53.5}{17} = 3.15$; every 3.15 parts of NH_4Cl contains one part of NH_3 . This solution can be *diluted*, as you may require a solution containing $\frac{1}{100}$ of a milligram in each C. c.

4. *The distilled water* that is required for making up the solutions, and the various standards of ammonia, must always be examined to see that they are free from ammonia. All the apparatus must be perfectly clean, and, if possible, *kept only for this purpose*. It is well to have a room set apart for the analysis of water away from the working laboratory and from the fumes of ammonia. It is well to have one C. c. pipette graduated into one-tenth C. c., and to have a series of pipettes holding 1, 2, 3, 5, 10, 25, and 50 cubic centimeters. The Nessler glasses should be of *white* glass, and graduated into 50, 100, and 150 C. c. each.

One-half liter of the water is placed in a *clean* flask that is connected with a Liebig condenser. Heat is applied by means of a sand bath, and the distillate is collected in the Nessler tubes. When fifty C. c. of the distillate have come over, the Nessler tube is changed. The first fifty C. c. should be *Nesslerized* by adding two C. c. of Nessler reagent, and noticing the *color* produced. The next step is to get the *same depth* of color by adding a *measured volume* of the standard solution of dilute ammonia to fifty C. c. of *pure* distilled water to which two C. c. of Nessler's solution has been added. The tubes are placed side by side upon a sheet of *white* paper, and the depth of color compared by looking

down the tubes, or standing off a few feet and looking obliquely through the liquid. When the solutions are of equal depth of colors, the Nesslerizing is accomplished, and the amount of ammonia in the unknown solution equals the amount of ammonia added from the standard solution. The distillation is continued until 200 C. c. have come over. The first 50 C. c. contain three-fourths of the total *free* ammonia, but it is well to Nesslerize each fifty C. c. as it comes over, when the *sum* of four tests will be the *free ammonia*. The distillation is stopped for a few moments, fifty C. c. of the permanganate solution is added, and the distillation continued. Each fifty C. c. is Nesslerized as it comes over until it is *free from ammonia*, which usually requires 150 C. c. The sum of these is the *albuminoid ammonia*. The subtraction for the ammonia in the permanganate solution should be made here, if required.

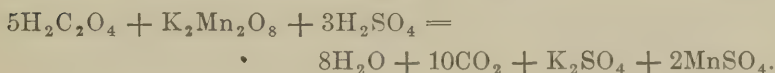
289. The method by Forchhammer, of oxidizing the organic matter by $K_2Mn_2O_8$, is now employed, with various modifications :



This *available oxygen* is, by some, made directly the basis of comparison. As regards the time during which the sample of water should be exposed to the action of the permanganate, authorities differ somewhat. Tidy is in the habit of registering the reduction (in the absence of iron and H_2S), which occurs in *three minutes*, as due to nitrites. The operation is continued for one hour, and three hours at a temperature of $60^\circ F$. *It is well in all the reports to state the time*. The operation is usually conducted as follows: 100 C. c. of the water is placed in a flask of 200 C. c. capacity, and to it fifteen C. c. of dilute H_2SO_4 (one acid and three water) is added. From a burette, 10 C. c. of centi-normal permanganate solution is added, and the flask is heated to boiling for *fifteen minutes*. Should the color disappear, more permanganate is added until the color remains permanent during the boiling. Ten C. c. of a centi-normal solution of oxalic acid is added, and the mixture again heated. The red color is

discharged. Enough of the centi-normal permanganate is again added to give it a *red tinge*. The same quantities of oxalic acid and permanganate should *exactly* neutralize each other in color, and the excess of the permanganate over the oxalic acid indicates the amount required for oxidation of the water. The number of C. c. of permanganate in excess is multiplied by .3135 (the amount of milligrams of $K_2Mn_2O_8$ in each C. c. of centi-normal solution). Multiplying the result by five, we get the number of milligrams of organic matter in 100 C. c. of the water tested: multiplying the number of C. c. of $K_2Mn_2O_8$, read off directly, by 15,675, you obtain the number of milligrams in a liter. Drinking water should not contain more than fifty milligrams of organic matter per liter (equal to 2.9 grains per gallon).

The action of permanganate upon oxalic acid is as follows:



The molecular weight of $K_2Mn_2O_8$ is 313.56; $\frac{1}{10}$ of this amount, in grams in a liter of water, is a normal solution; $\frac{1}{100}$ is a deci-normal; $\frac{1}{1000}$ is a centi-normal = .3135 grams to a liter. Each C. c. will contain .3135 milligrams of $K_2Mn_2O_8$. This is multiplied by an *arbitrary constant* five (Kubel, Woods, Mohr). (Frankland uses 2.38 times for river water, and 5.8 times for well water.)

$.3135 \times 5 \times 10 = 15.675$ for a liter (100 C. c. is $\frac{1}{10}$ of a liter).

This method is rapid, easy of execution, and reasonably correct. It is very difficult to handle with any certainty the organic matter in water, owing to the decompositions that may take place from the fermentation of albuminoids, peptones, amido-derivatives of mono and bibasic acids of the fatty series (as valerianic, butyric acids); from the aromatic series (as cresol, indol, etc.) The fats may split up into glycerin and fatty acids, which may be transformed by oxidation into acids of lower groups; from the carbohydrates there may be formed by fermentation a number of alcohols, aldehydes, and acids of

the fatty series. Waters in connection with cesspools may contain the constituents of urine and their products of decomposition. Where the residues of vegetation are decaying, substances of the humus class may be present; hence the organic impurities of water may differ in their properties. Fixed and volatile bodies, permanent and unstable compounds, may occur together; hence there cannot exist any simple method for determining the total amount of organic matter in water.

290. The sulphates are determined by heating 100 C. c. of the water to boiling, adding a few drops of HCl and a slight excess of BaCl_2 . The precipitate is washed, ignited, and weighed. The BaSO_4 , multiplied by the factor .34331, gives the amount of SO_3 ; or by .42051, gives the amount of H_2SO_4 . This multiplied by ten gives it for a liter.

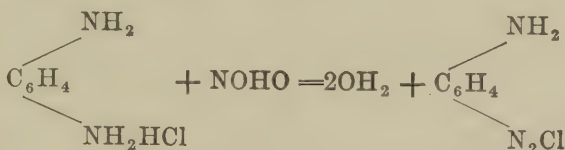
291. The nitrates. Seventy C. c. of water to be tested is mixed with an equal volume ten per cent. solution of *pure* sodium hydroxide, and boiled briskly until reduced to one-half its volume; it is then made up to its original bulk with *pure* distilled water. A piece of aluminium foil three or four inches square, rolled around a clean glass rod to keep it from floating, is added, and the bottle set aside for three or four hours. The liquid is distilled in a small retort, and the distillate Nesslerized. The ammonia is to the nitric acid as seventeen is to sixty-three. It is well to have the bottle protected from ammonia by a calcium chloride tube filled with pumice or glass beads wetted with HCl or H_2SO_4 to prevent any NH_3 from the atmosphere from entering the apparatus. The water residues may be tested *qualitatively* for nitrates by heating one part of carbolic acid with four parts of sulphuric acid; the mixture is diluted with an equal volume of water. When boiled with nitrates, it gives a *brownish-red* color.

292. The nitrites. The reagents required are: (1) Dilute sulphuric acid (one of acid two of water); (2) five grams of meta-phenylene-diamine in an acid solution (HCl or H_2SO_4) of water made up to a liter; (3) .406 grams of pure silver nitrite

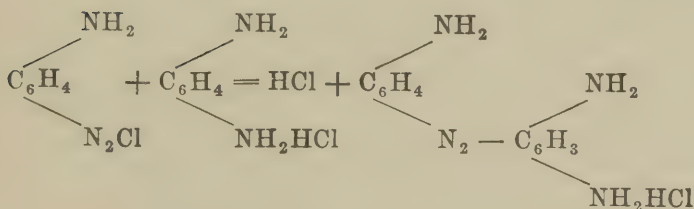
are dissolved in boiling distilled water, when pure potassic or sodic chloride is added till no further precipitate of silver chloride occurs. Make up to a liter. When the silver chloride settles, dilute 100 C. c. of the clear liquid to a liter. Keep in the dark and in bottles completely filled. One C. c. = .01 milligram of N_2O_3 . The color it gives is a "*Bismarck brown*."

One hundred C. c. of the water to be tested is poured into a Nessler tube and one C. c. each of the dilute sulphuric acid and the solution of meta-phenylene-diamine consecutively added. The color produced is compared with a standard solution of the nitrite, as in the estimation of ammonia by the Nessler test. (This detects one part in 30,000,000.)

The reaction which takes place is thought to be expressed as follows:



Meta-amido-diazobenzene-chloride.



Triamido-azobenzene hydrochlorate (yellow coloring matter).

293. The following method is sometimes used. The reagents are: (1) The standard solution of silver nitrite above mentioned: $2\text{AgNO}_2 = \text{N}_2\text{O}_3 + \text{Ag}_2\text{O}$ or $\frac{2\text{AgNO}_2}{\text{N}_2\text{O}_3} = 4.06$ (introducing the molecular weights and performing the division); .406 grams of AgNO_2 gives 100 milligrams of N_2O_3 to the liter.

(2) A solution of sulphanilic acid. (3) A solution of naphthylamine in alcohol. One hundred C. c. of the water is acidulated with *pure* sulphuric acid; six or eight drops of sulphanilic acid are added; in a few minutes afterward, a few drops of a colorless solution of naphthylamine, when a *magenta red* color is produced. This color can be compared with a known quantity of silver nitrite as above described.

294. To convert parts per 100,000 into grains per gallon, multiply by .7. To convert grains per gallon into parts per 100,000, divide by .7. To convert grams per liter into grains per gallon, multiply by 70. Milligrams per liter is the same as parts per 1,000,000.

295. Notes:—

When the *free ammonia* exceeds .08 parts per million, it is quite sure to come *from urea*. In such a case the water will be loaded with *chlorides*. Good water should not contain *more than one part of free ammonia in 10,000,000*.

A large quantity of *albuminoid ammonia*, with little *free ammonia*, and absence from chlorides, indicates vegetable contamination. Good water should not contain *more than one part in 10,000,000*.

Human urine contains 824 parts of sodic chloride, or about 500 parts of chlorine in 100,000 parts. Water containing more than twenty milligrams of chlorine per liter (1.4 grains per gallon), derived from other sources than a saline subsoil should be rejected. It should not contain *more than one part in 100,000*.

The hardness of water should not be more than .2 gram of CaO per liter, or its equivalent of magnesium.

Water should not contain over fifteen parts of nitric acid per 1,000,000.

Water containing nitrites is apt to be due to sewage contamination, and any thing over .1 milligram per liter can be *suspected*. In estimating the total solids, it may be necessary to dry the residue at 110° C. to 120° C. before it is weighed. Care must be taken not to expel the carbonic acid, etc.

In *every* case of doubt a *blank* experiment should be made with *pure* distilled water under the *same conditions as the experiment*.

The solution of meta-phenylene-diamine can be decolorized, if necessary, by filtering through animal charcoal.

The silver nitrite can be made by precipitating silver nitrate with potassium nitrite, washing and drying.

The search for impurities in water will vary largely with the purpose for which the water is to be used; *e. g.*, for steam boilers, for laundries, or for a beverage. In the last case, such impurities as may have come from animals, and especially from diseased animals, should be sought after with scrupulous care, and if found, the water should at once be rejected as unfit for use.

CHAPTER VII.

POISONS—PTOMAINES, ETC.

296. The name “ptomaines” has been given by Selmi to bodies which have been detected in exhumed corpses, and resemble the vegetable alkaloids in their chemical reactions and physiological effects. These ptomaines are usually produced in bodies which, after a brief exposure, have been excluded from the air, for they occur in buried bodies, sausages, and tinned foods, and, in most, though not in all, cases, the production is in the internal portion.

Panum and Schwenigner have investigated the poisonous effects produced by food in certain stages of putrefaction or fermentation, and have found that different physiological actions are produced at different stages of decay; while Sonneschein and Zuelzer found in the fluid produced by anatomical maceration an alkaloid which resembles atropine in its action. The poisons of putrefied sausages produce similar effects, and also contain other bodies which cause tetanic symptoms. In many cases of poisoning by food, as, for instance, by cheese, the bad effects were not due to vegetable growths or to microscopic organisms. Many individuals have derived from the putrefaction of maize, a body that will produce tetanic symptoms. The relation of these products of putrefaction to certain diseases is evident from the fact that Sonneschein's alkaloid is found in the bodies of patients dying of typhus fever, and many persons poisoned by decaying food show marked typhus symptoms.

It becomes a matter of grave importance to the chemist to be able to distinguish between these poisonous bodies, which are the

result of putrefactive processes, and the vegetable principles, which, when administered, may produce death.

Some chemists have thought it possible that conine might be produced in animal substances, as from butyric acid and ammonium, with the separation of $2\text{H}_2\text{O}$, thus :



It is very doubtful if the synthesis of such bodies is a common occurrence. The chemical constitution of most of the characteristic ptomaines are (according to Brieger, 1885) diamines, and are more simple in composition than the vegetable alkaloids. They are, generally, quite strong reducing agents. Brieger says there is no distinctive test for them. There is, therefore, all the uncertainty about the properties of these bodies which is inherent in conclusions based upon reactions on minute quantities, and in physiological experiments undertaken with substances the *purity of which is doubtful*.

297. The general method of Selmi was to make an alcoholic extract, after the method of Stas ; to filter, and evaporate the alcoholic extract in a vacuum, at from 30° to 35° C. An aqueous solution was then made from this extract, and the solution shaken up with solvents (the solution itself remaining acid, or rendered alkaline with $\text{Ba}(\text{OH})_2$). From both the acid and the alkaline liquids, ptomaines were extracted by means of ether, that differed in their chemical reactions and physiological properties. Ptomaines were also extracted by chloroform and amylic alcohol.

Ptomaines from fatty matters are extracted by washing the fatty substance with water acidulated with sulphuric acid, and then extracting the solution with ether, first acting on the acid liquid, and then on the same alkalized by $\text{Ba}(\text{OH})_2$.

298. Tyrotoxinon or "cheese poison." It has been long known that ice cream, milk, cheese, etc., have given rise to poisonous symptoms. Prof. Vaughan has recently extracted a diazobenzin ($\text{C}_6\text{H}_5\text{:N:N}$) compound, as follows: The filtrate

from the milk, or the filtered aqueous extract of cheese, is neutralized with Na_2CO_3 , and then shaken up with half its volume of *pure* ether; after the separation of the ether, it is allowed to evaporate spontaneously in a suitable vessel. The residue from the ether is dissolved in water, and again extracted with ether. The aqueous solution of the ether is added to a saturated solution of KHO, and evaporated on the water bath ($\text{C}_6\text{H}_5\text{N}_2\text{OK}$) (at 100°C . it may explode). Mix a few drops of pure sulphuric acid with pure carbolic acid, on a white porcelain dish (it should remain colorless); now add a few drops of the residue left after the spontaneous evaporation of the ether. If the tyrotoxinon is present, a *yellow to an orange color* will be produced.

299. A poison is any animal, vegetable, mineral, or gaseous substance which, when applied externally, or taken into the stomach or circulatory system, causes such a change in the animal economy as to produce disease or death. Its action may be chemical or physiological. The physiological may be corrosive, irritant, or neurotic. The chemical poisons are organic and inorganic.

The action of the poisons may be local or remote—local, when confined to the part to which the poison is applied, as in the case of strong acids, etc.; remote, when the action extends to distant organs. Poisons have a wonderful power of selecting organs or tissues peculiar to themselves—strychnine, the spinal cord; opium, the brain; hydrocyanic acid, the lungs; digitalis, the heart. Death is, in most cases, due to remote action. The action of the poison on the system may be modified by—

1. The quantity.
2. The molecular or physical condition of the poison—most active as a gas or vapor, next as a liquid, and least as a solid.
3. Chemical combination. (a) It may be increased as when morphine is given with acetic or hydrochloric acid. (b) It may be diminished, as when sulphuric acid and caustic soda are given together.
4. Mechanical mixture, when its action may be delayed.

5. The manner of giving it, by the mouth, wound, etc.
6. The habits of the person; and closely connected with this is the idiosyncrasy of the person.
7. The condition of the person as to health. It is retarded by sleep and food.

The evidences of poisoning are (1) symptoms, (2) post mortem appearances, and (3) chemical analysis. As the symptoms of many poisons and diseases are alike, the burden of proof remains for chemical analysis.

300. Before the chemical analysis is taken up, a few words might be said as to general treatment:

1. Get the poison out of the system as soon as you can.
2. If you cannot remove it, neutralize it, if possible.
3. Assist its elimination by cathartics and diuretics.
4. Treat the symptoms, as they arise, upon general principles.

The first may be secured by emetics and the stomach pump. The second requires antidotes, of which there are three classes, chemical, mechanical, and physiological. In general terms, the following are considered as the requisites of an antidote:

1. It should be easily accessible.
2. It should be capable of being administered by any one.
3. It should be capable of being taken in *very large quantities without injury*.

The organs examined are usually the stomach and the liver.

301. 1. It is recommended for the student to take the pure poison (say strychnine), and see if he can confirm it by all the tests given in the book.

2. To add it to food, making it as nearly as possible like the contents of the stomach, and then to try to *separate and identify the poison*.

3. To take some small animal, as a dog or cat, and administer a poisonous dose, and to notice the following: (a) The

quantity taken, which is always weighed. (b) The length of time before symptoms of poisoning began. (c) The duration of the symptoms until recovery or death. (d) The character of the symptoms. (e) The post mortem appearances.

The first requisite of every analyst is *cleanliness*. See that everything is *absolutely clean* by washing it first with acid, and rinsing it with water three or four times; then again washing it with an alkali (as NaHO or KHO), and again rinsing with water three or four times; and lastly, with distilled water several times; also, *test the purity of every reagent used*. In almost every step of the work you may find difficulties which it is impossible to predict, the remedies for which must be suggested by your general knowledge of chemistry. The inorganic poisons are generally quite easily detected, and usually will not give any trouble. The organic poisons are detected with difficulty, and more readily pass off, in some cases leaving no traces behind. For this reason they are first sought. In all cases, only one-third to one-half the contents of the stomach, or other organ, is taken; the rest is kept in case of any accident in the work.

Before beginning the work of the analysis, it is well to note accurately the manner in which the samples have been packed; whether the seals have been tampered with; whether the vessels or wrappers themselves were likely to contaminate the articles sent; and then to make a very careful observation of the appearance, smell, color, and reaction of the matters, not forgetting to take the *weight* if solid, the *volume* if liquid. In short, *find out all you can about the case*. In examining the stomach, first of all empty the contents into a *clean* glass vessel; open the stomach, and spread it out on a clean, white plate, and note in writing its internal appearance. Examine it very carefully with a good glass, especially the surface. In some cases it may be required to have it photographed. You may sometimes find pieces of leaves, fruit, seeds, and the like, or powders that adhere to the walls of the stomach. A knowledge of the food eaten may be of importance. Any or all of these may give a clue to the cause of death. Whatever is found, let it be carefully preserved.

302. The following is a general process for the separation and identification of poisons:

One-half the contents of the stomach is placed in a strong flask, and if neutral or alkaline, it is feebly acidulated with tartaric acid. The flask containing the substance or liquid under examination, may be gently heated on the water bath. Volatile substances, prussic acid, hydrochloric acid, phosphorus, etc., if present, will distill over, and can be carefully examined by redistillation and the various appropriate tests. When *all* the volatile substances have passed over, the substance is dried. This can be effected by a Bunsen filter pump, and dried over sulphuric acid. When *dry*, it is reduced to a coarse powder and extracted with petroleum ether (benzin) in a large Soxhlet apparatus. The petroleum extract, when evaporated, leaves the fatty matter containing traces of some of the alkaloids. When this is treated with dilute sulphuric acid, the alkaloids are dissolved out, leaving the fat behind. The substance remaining is practically free from water and fat. It is digested in the cold with absolute alcohol for three hours, and the alcohol is filtered off and allowed to evaporate spontaneously. It can now be treated with ninety per cent. of hot alcohol, filtered, and the filtrate evaporated. The dry residue is exhausted with ether. The ether and water being driven off, it can be treated with water, and the extract examined for alkaloids and organic acids.

303. A few metallic poisons (as corrosive sublimate) are soluble in alcohol, and must not be overlooked. The residue, after being acted upon by petroleum, alcohol, ether, etc., is placed in a retort, and distilled once or twice to dryness with a known quantity of strong hydrochloric or sulphuric acid. The residue is carbonized and treated with dilute hydrochloric acid, filtered, and tested with H_2S for Zn, Cu, Pb, etc. See Nos. 158, 178. The distillate that came over (before it was carbonized) is also tested by H_2S . It is customary to take one-third for organic poisons, one-third for inorganic, and to keep one-third in case of accident. This method does not give good results with phosphorus or oxalic acid. The phosphorus can be *distilled in the dark* (in the

absence of alcohol or ammonia), and condensed with a Liebig's condenser. One part in 200,000 can be shown in this way. Bisulphide of carbon can be used to dissolve it out if in large quantities. The oxalic acid can be detected by digesting the substance or fluid with HCl, filtering, neutralizing with NH_4HO , and allowing it to precipitate. The filtrate is treated with acetate of lime. The first precipitate contains all the oxalic acid in combination with lime; the second, that which was in the free condition. These precipitates are washed with acetic acid, and identified.*

As but *one poison* is usually found in the above solutions of ether, alcohol, chloroform, etc., no special trouble will be found in identifying it.

304. In applying a reagent to a solution of an alkaloid, add a drop or two of the reagent to an equal quantity of the solution of the alkaloid on a glass slide placed over black paper. A magnifying glass will also be found useful.

The following general reagents will be found useful:

305. Iodine in potassium iodide solution (Wagner, 1866). Twenty grams of iodine and fifty grams of potassium iodide in a liter of water. The precipitates are *brown* and *flocculent*. A very slight addition of the reagent is sufficient. The alkaloid may be recovered by washing the precipitate and dissolving it in an excess of aqueous sulphurous acid and evaporating on the water bath. The sulphurous acid expels the hydriodic acid, the alkaloid remaining as a sulphate. In cases where the alkaloids are expensive, this method can be used.

* The alkaloids are divided into two divisions, volatile and non-volatile. To the first belong *nicotine* and *conine*. The second has three subdivisions: first, those that are precipitated by potash, soda, or a solution of their salts, and redissolve in an excess of the precipitant—*morphine* is the most important one; second, those that are precipitated by potash or soda, but do not redissolve to any great extent by an excess of the precipitant, and are precipitated by bicarbonate of soda from acid solutions—*narco-tine*, *quinine*, and *chinchonine*; third, those that are precipitated by potash or soda, and do not redissolve to any great extent by an excess of the precipitant, but are not precipitated by a bicarbonate of the fixed alkaline metals—*strychnine*, *brucine*, *veratrine*, and *atropine*.

306. Potassium mercuric iodide (Mayer's solution). Dissolve 13.525 grams of crystallized mercuric chloride in a beaker of water containing 300 C. c. of water; in another beaker, with the same amount of water, dissolve 49.680 grams of potassium iodide. Mix the solutions, and make up to a liter with water. It is applied only in acidulous (HCl or H_2SO_4) solutions. The solution to be tested should not contain alcohol or acetic acid. The precipitate is *curdy* or *flocculent*, and generally a *yellowish-white* color. The alkaloid can be reclaimed from the precipitate by treating the washed precipitate with stannous chloride and potassium hydroxide to strong alkaline reaction, and then exhausting with ether, chloroform, or benzene as a solvent for alkaloids.

307. Phosphomolybdate (Sonnenschein). The yellow precipitate formed on mixing acid solutions of ammonium molybdate and disodic hydric phosphate (the ammonium phosphomolybdate) is well washed, suspended in water, and heated with sodium carbonate until completely dissolved. The solution is evaporated to dryness, and ignited till all the ammonia is expelled, sodium being substituted for ammonium. If the molybdenum is reduced (blackening), the residue is heated with nitric acid, and again heated. One part of the residue is dissolved in ten parts of water, with the addition of *strong* nitric acid. It must be kept from contact with vapors of ammonia, both during its preparation and while kept for use. The colors of the precipitates are *orange yellow* to *brown yellow*. Acidified solutions yield the best results. Most of the precipitates are amorphous, and are soluble in ammonia. Alkaloids that are strongly reducing give some shade of *blue*. If the precipitated alkaloid is treated with potassium or sodium hydroxide solution, it can be dissolved out with ether, benzene, amyl alcohol, or chloroform.

308. Potassium cadmium iodide (Marme, 1866). Saturate a boiling concentrated solution of potassium iodide with cadmium iodide, and add an equal volume of a cold saturated solution of potassium iodide. It precipitates the aqueous solutions,

acidified with sulphuric acid; soluble in excess of the precipitant or in alcohol. In dilute solutions, precipitation is apt to occur. The precipitate is at first amorphous, but becomes crystalline. The alkaloids can be recovered from the precipitates as directed for potassium mercuric iodide.

309. Potassium bismuth iodide (Dragendorff, 1866). Prepared from bismuth iodide, in the way directed for the last named reagent. It can be used for aqueous solutions of alkaloid salts when strongly acidified with sulphuric acid.

310. Picric acid (Hager, 1869). In a *dilute* alcoholic solution. The precipitates form best from sulphuric acid solution. They generally have a *yellow* or *yellowish-white* color. The alkaloids can be recovered from their picrate precipitates by adding an alkaline solution and exhausting with water, or by evaporating to dryness with a solution of potassium or sodium carbonate, and extracting with alcohol.

311. Concentrated sulphuric acid containing molybdic acid (Frøehde's reagent). A solution of .001 gram of molybdic acid or alkali molybdate in one C. c. of concentrated sulphuric acid, freshly prepared by the aid of heat, and used when cold.

312. Metatungstic acid (Scheibler, 1860). Add phosphoric acid to a solution of tungstate of sodium as long as a precipitate is formed, and dissolved. The precipitates are *white* and *flocculent*.

313. Tannic acid (Berzelius) in solution with eight parts of water and one part of alcohol. The precipitates are *white* to *yellowish*, and are soluble in ammonia.

314. Platinic chloride (see No. 79) and **auric chloride** (see No. 69) are sometimes used; also the *mineral acids*. The color tests may vary with the *impurities* of the alkaloid or reagent, with the *concentration*, *time*, and *temperature*. In case of any doubt, compare it with the known *alkaloid in question*, under the same conditions of temperature, etc.

Never jump to conclusions on the result of your analysis.

315. Strychnine ($C_{21}H_{22}N_2O_2$) was discovered in 1818 by Pelletier and Caventou. It is found in the seed of *Strychnos nuxvomica*, *S. Ignatii*, *S. Colubrina*, and *Upas Tieute*, of the natural order *Loganiaceæ*. The quantity varies from one and five-tenths to four per cent. Brucine is often used to adulterate it, and it occurs with it in the bean. Five grams of the finely powdered nux-vomica seeds are packed in the percolator of a continuous extraction apparatus, and treated with forty C. c. of alcoholic chloroform, containing twenty-five per cent. of alcohol, for two or three hours. The alcoholic solution is treated with twenty-five C. c. of ten per cent. dilute sulphuric acid. The acidulous watery solution is separated from the chloroform and made alkaline with ammonia, and shaken up with twenty-five C. c. of chloroform; the chloroform is gently evaporated, and the weighed residue heated to $100^\circ C.$, on the water bath. This gives the total alkaloids.

1. The brucine can be separated from strychnine by precipitating the sulphates with ferrocyanide. The *strychnine is precipitated*; brucine is not precipitated *unless concentrated*.

2. When treated with twenty-one per cent. (by weight) alcohol, brucine is dissolved; strychnine undissolved, or but slightly dissolved. Nitric acid gives *blood red* with brucine; strychnine, *no color reaction*.

The best solvent is chloroform. The medicinal dose is from one-thirtieth to one-twelfth of a grain; the smallest fatal dose is from one-fourth to one-half a grain. When taken in poisonous doses, the symptoms come on suddenly. The patient has violent tetanic convulsions; the pain is intense; the pulse rapid; the mind clear; vomiting is uncommon. The post mortem appearances are engorgement of the lungs, congestion of the brain and spinal cord, the fingers are clinched, and the body opisthotonos. The treatment is by emetics and the stomach pump. The use of chloroform, tannic acid, opium, camphor, and chloral hydrate has been recommended.

Strychnine is remarkable for its stability under ordinary influences of decomposition.

316. Tests:—

1. Mayer's solution gives a precipitate.

2. Sonnenschein's reagent gives a precipitate which dissolves in ammonia without coloration.

3. Alkali hydroxides give crystallizable precipitates; soluble in excess only in the case of ammonia.

4. It is white, and has an intensely bitter taste, perceptible in a solution diluted to 600,000 to 700,000 parts. The bitter taste is followed by some degree of metallic after taste. When heated on Pt foil, it melts and burns like resin, with a black, smoky flame.

5. Most specimens of strychnine when dissolved in nitric acid give a red color, due, possibly, to brucine; if dissolved with sulphuric acid, it is colorless. If to this solution oxygen be added, or any oxidizing agent, as a small crystal of bichromate of potash, ferricyanide of potassium, black oxide of manganese, or peroxide of lead, there is a beautiful play of colors—purple, violet, and crimson. Black oxide of manganese is the best reagent for the above, and potassium bichromate is the worst. Dr. Letheby uses a galvanic battery to generate the oxygen. Curarine gives the same reaction with sulphuric acid and potassium bichromate; but curarine is colored by sulphuric acid alone, while strychnine is not*. Morphine *interferes* with this reaction. Sulphomolybdic and iodic acids produce no immediate change of color in strychnine, while they do in morphine. (To separate strychnine from morphine, make it alkaline and treat with chloroform; it dissolves the strychnine but not the morphine; or absolute alcohol, which dissolves the morphine but not the strychnine.) The fact that morphine is given by physicians should caution the student to be careful in distinguishing between them.

6. Sodium bicarbonate, or potassium sulphocyanate, or mercuric chloride, or iodide of potassium produces a white precipitate.

* Curarine gives, with sulphuric acid, a red color; strychnine gives none. Curarine may be separated from strychnine by means of benzene, in which the former is insoluble. Cod liver oil gives a similar reaction; distinguished by the taste. Aniline, pyroxanthine, papaverine, narceine, veratrine, and solanine belong to this list.

8. Dr. Hall's physiological test is made by injecting a dilute solution of strychnine into the thorax or abdominal cavity of a frog, causing tetanic convulsions. Locally there is but slight irritation. Its tetanic effects are due to its action on the gray nerve tissue of the spinal cord. Many of the tests are delicate when examined with a microscope.

317. Brucine ($C_{23}H_{26}N_2O_4$) was discovered by Pelletier and Caventou in 1819. It has been thought by some to be a dimethoxy-strychnine, $C_{21}H_{20}(OCH_3)_2N_2O_2$, and to be capable of being converted into strychnine(?). Brucine is found with strychnine in the *Strychnus nux vomica*, *S. Ignatii*, *S. Colubrina*, and *Upas Tieute*, of the natural order *Loganiaceæ*. The best source of brucine is the *false angustura* bark, which contains but little strychnine. The effect of brucine is similar to that of strychnine, but requires ten or twelve times the amount of strychnine to produce the same effect. It is excreted far more rapidly than strychnine—so rapidly that when given by the stomach to animals it produces little effect. It is soluble in alcohol, chloroform, benzene; almost *insoluble* in ether. In separating it from organic mixtures, see strychnine. The ordinary salts of brucine are soluble in water and in alcohol, but not in ether. The symptoms of brucine are like those of strychnine, but they come on more slowly and are less violent. The mode of treatment is the same for both poisons.

318. Tests:—

1. The *general reagents for alkaloids* give the customary precipitates with brucine

2. The physiological test of brucine, with a frog, is, qualitatively, nearly the same as that for strychnine, but larger quantities are required.

3. When brucine is treated with nitric acid (sp. gr. 1.42), it gives a *blood red color*; if it is heated, it changes to yellow. When cold, and a trace of protochloride of tin is added, the color changes to a deep purple; an excess of acid or of tin bleaches it.

4. Bichloride of platinum gives a *yellow precipitate* of the double chloride of platinum and brucine, decomposed by caustic alkalies; insoluble in acetic acid. The chloride of gold gives a somewhat similar *amorphous* precipitate; sparingly soluble in acetic acid. Caustic alkalies blacken it.

5. When mixed with sulphuric acid and bichromate of potash, orange, green, and yellow tints are produced in turn, due to the reduction of the chromium.

6. If, to a solution of brucine in strong alcohol, a little methyl iodide is added, in a few minutes circular rosettes of methyl brucine iodide, $C_{23}H_{25}(CH_3)N_2O_4HI$, form.

319. Igasurine is an alkaloid as yet but little studied. It is said to be poisonous, its action being similar to that of strychnine and brucine, in activity standing midway between the two. It is obtained from the boiling-hot watery extract of nux-vomica seeds after precipitating the strychnine and brucine by lime and then evaporating the filtrate.

320. Morphine ($C_{17}H_{19}NO_3$) was discovered by Sertürner in 1816. It is one of the poisonous alkaloids of opium, good opium yielding from six to fifteen per cent. of the alkaloid. Hesse (1872) presented a division of the opium alkaloids by treating them with *pure* sulphuric acid:

1. Morphine, pseudomorphine, codeine, gave *dirty dark green*.

2. Laudanine, codamine, laudanosine, gave *dirty red violet*.

3. Thebaine (?), cryptopine, protopine, gave *dirty green to brown green*.

4. Papaverine gave *dark violet*.

5. Narceine, lanthopine, gave *black brown to dark brown*.

6. Narcotine, hydrocotarnine gave *dirty red violet* of a different shade from (2) above.

The salts of morphine are, for the most part, crystalline, and are all bitter, neutral, and poisonous. They are insoluble in ether, chloroform, benzene, or petroleum ether. It is a decided

base, and neutralizes strong acids. The medicinal dose is one-fifth of a grain. The smallest fatal dose is one grain. It is about six times as strong as good opium. Drowsiness and stupor are the first symptoms; pulse, weak; breathing, slow and almost imperceptible; the pupils, in most cases, contracted. When large doses (poisonous) are given, these symptoms are sometimes attended with convulsions. The post mortem appearances have nothing characteristic, except, in some cases, the peculiar odor of opium. During treatment, keep the patient constantly aroused by any means. The poison should be eliminated by emetics and the stomach pump. In some cases the magneto-electricity is used with good effect to prevent insensibility; solutions of iodine, bromine, and tannic acid have been recommended. Strong tea or coffee is the best drink. Ammonia can be applied to the nostrils in case of a collapse. The existence of opium is determined by the presence of morphine and meconic acid.

The aqueous solutions of morphine can be concentrated on the water bath, better under diminished pressure, at 75° C. The residue is treated with hot alcohol. The acidified aqueous solution may be purified from other alkaloids by being treated with benzene, ether, and chloroform. The liquid is made alkaline with ammonia and treated with amyl alcohol to dissolve out the morphine.

321. Tests:—

1. Nitric acid gives, at first, a bright red, then an orange red color. Chloride of tin does not decrease the color, differing from brucine.
2. Dissolve ammonium molybdate in strong sulphuric acid (and it should be made as required for use). It gives with morphine, or its salts, a reddish purple or crimson red color. This changes to a green, and ultimately to a sapphire blue (Frøehde's reagent).
3. If iodic acid and bisulphide of carbon are mixed together no change occurs; if morphine (solid or solution) is added,

iodine is separated from the iodic acid, and dissolves in the bisulphide, coloring it pink or red. Of course, a solution of starch will do as well, giving a blue color.

4. The reducing power of morphine is also shown by treating a drop of neutral ferric chloride with a drop of a dilute solution of potassium ferricyanide; a blue color indicates morphine. Narcotine, brucine, and the ptomaines, give this reduction.

5. Morphine, treated with concentrated sulphuric acid and potassium chromate, gives a green color, due to the reduction of the chromium.

6. Neutral ferric chloride gives a blue color with morphine or its salts.

7. The general qualitative reagents for alkaloids all give tests with morphine.

8. Add a drop of pure sulphuric acid to the dry residue of morphine; with a glass rod, moistened with nitric acid (sp. gr. 1.42), touch the moistened residue, when a red to violet color indicates morphine. Potassium nitrate can take the place of nitric acid above.

322. Meconic acid ($\text{H}_2\text{C}_7\text{HO}_7$). Found only in opium (three to four per cent.) It crystallizes in white, shining scales or small rhombic prisms. It is soluble in 115 parts of water, freely soluble in alcohol, slightly soluble in ether. It has a marked acid reaction, and an astringent taste. The meconates are nearly all insoluble in alcohol. It gives, with a solution of ferric chloride, *red color*; with acetate of lead, *yellowish-white color*. Nitrate of silver precipitates *yellow amorphous* meconate of silver; barium hydroxide precipitates *yellow meconate* of barium. The physiological action is thought to be similar to lactic acid. There is slight narcotic action on man. The alcoholic extract from organic fluids is made *feebly* acid with HNO_3 ; on filtration, the alcohol, after the addition of a little water, is distilled off, and to the remaining fluid a solution of lead acetate is added, and the whole filtered. The filtrate will contain any alkaloids; whilst meconic acid, if present, is with the lead on the filter. It is

washed with acetic acid to purify it. The lead salt is decomposed by H_2S , and the filtrate is tested with ferric chloride, or evaporated to dryness and weighed.

323. Codeine ($C_{18}H_{21}NO_3$) was discovered by Robiquet in 1832. Opium contains from one-tenth to one per cent. It is separated from morphine and narcotine by its solubility in water (eighty parts cold, seventeen parts hot), benzene, and ether. The anhydrous alkaloid melts at $150^\circ C.$, and solidifies to a crystalline mass on cooling. It has a strong alkaline reaction. It is odorless, somewhat bitter, and resembles morphine in its physiological action. The dose is from five-tenths to one grain (.032 to .065 grams). It is readily soluble in alcohol, ether, and chloroform (seven parts amyl alcohol, ten parts benzene); almost insoluble in petroleum benzin. Chloroform extracts it from alkaline solutions most readily.

324. Tests:—

1. Ammonia precipitates it after standing (not completely), potassium hydroxide, iodine in potassium iodide (brown), potassium mercuric iodide (white), potassium cadmium iodide (white), phosphomolybdic acid (yellow brown), tannic acid (white), mercuric chloride (crystalline), platinum chloride (yellow), gold chloride (brown).

2. Concentrated sulphuric acid dissolves it without color, becoming blue on warming. If a trace of nitric acid or ferric salt be added, the blue color is hastened.

3. Nitric acid (sp. gr. 1.2) dissolves it to a yellow liquid, which should not become red (difference from, and absence of, morphine).

4. It is distinguished from morphine by (1) the different form of its crystals (which are octohedral); (2) its solubility in boiling ether; (3) its insolubility in alkaline solutions; (4) not assuming a red color with nitric acid, (5) or a blue with ferric salts.

Morphine is artificially converted into codeine (Grimaux, 1881) by treatment with methyl iodide and fixed alkali.

325. Narcotine (Desrone, 1803). Opium contains from 1.3 to 10.9 %. It acts as a narcotic poison only in large doses (from 1.5 to 3 grams). It is distinguished and separated from morphine by its solubility in ether. It is soluble in 7,000 parts of boiling water; in 24 parts of boiling alcohol (96%); in 48 parts of boiling ether (sp. gr. .735); in 60 parts of acetic ether; in 2.7 parts of chloroform; in 300 parts of amylic alcohol; in 22 parts of benzene. Chloroform removes it from acid solutions. It can be obtained from the residue after treating opium with water, by treating with dilute HCl, precipitating with NaHCO_3 , extracting the precipitate with boiling 80% alcohol, and crystallizing.

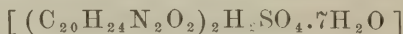
It is estimated gravimetrically or by Mayer's solution.

326. Tests:—

1. It gives precipitates with alkaline hydroxides, carbonates and acid carbonates, iodine in potassium iodide (brown), potassio-mercuric iodide (white), potassium sulphocyanate (amorphous). Other reagents not characteristic precipitates.

2. Concentrated sulphuric acid dissolves first colorless, then yellow. On heating, it becomes orange red, violet, dark blue, finally violet red. If a drop of HNO_3 is added to H_2SO_4 solution of narcotine, a red color is produced.

327. Quinine ($\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2$). (Pelletier and Caventou, 1820.) It has a bitter taste. It is poisonous to the *lower forms* of animal life. It is excreted *in the urine* to the extent of seventy to ninety-six per cent. of the amount taken. It sometimes appears in one hour after being taken, and disappears in about forty-eight hours. It is found in the liver. The bisulphate is more soluble than the sulphate. It has a decided alkaline reaction. The normal salts are neutral. The sulphate



is soluble in thirty parts of boiling water, in three parts of boiling alcohol, in forty parts of glycerin, in one thousand parts of chloroform, and slightly in ether.

Quinine salts, with mineral acids containing oxygen, exhibit blue fluorescence in their aqueous solutions. The bisulphate

shows this better than the sulphate. Other alkaloids of cinchona show this reaction. Quinine is very nearly separated from strychnine and morphine by its solubility in ether, partially separated by its solubility in ammonia. The sulphate of quinine is approximately separated from atropine and morphine by the difference of solubility in water. Kerner's method of identification is as follows: A certain quantity of the sulphate of the alkaloid is dissolved in a certain quantity of water, and then the water of ammonia is added gradually until the precipitated alkaloid is redissolved. The quantity of the ammoniacal liquid necessary to produce this effect, indicates inversely the solubility of the alkaloid. Quinidine requires from ten to eleven times more of the ammoniacal liquid than quinine; cinchonidine from twelve to thirteen times more; while cinchonine is not dissolved by a much larger proportion than is required by either of the others, and, though when mixed in very small proportion with quinine it is dissolved at first, yet it afterwards separates on standing. This test is now official.

328. Tests:—

1. Treated with fresh *chlorine water* or *bromine water*, not in excess, or well diluted, and then with *ammonia* to alkaline reaction, *green precipitate*, dilute solutions, green solution (Thalleioquin test). If ferricyanide of potassium be added after the Cl or Br, and then ammonia, a *red color* is obtained. Quinidine, diquinicine, quinicine, hydroquinine, and hydroquinidine give the above reaction, while cinchonidine and cinchonine *do not give it*.
2. Alkaline hydroxides and carbonates precipitate quinine.
3. The general reagents give precipitates with quinine.

329. Veratrine ($C_{37}H_{53}NO_{11}$) was discovered by Meissner in 1819. It is an alkaloid, or mixture of alkaloids, prepared from the seeds of *Asagracea officinalis*. The seeds are treated with alcohol, and the alcohol recovered by distillation. The residuary liquid contains veratrine with veratric acid. The resins are precipitated with water, and filtered; ammonia is added to the

filtrate. Veratrine is precipitated. It is purified by recrystallization. It is a white or grayish-white amorphous powder with an acrid taste. It leaves a numbness on the tongue, and is highly irritant to the nostrils. It has a feebly alkaline reaction. It is soluble in three parts of alcohol, six parts of ether, two parts of chloroform, ninety-six parts of glycerin. When heated, it melts; at higher temperatures it chars and is wholly volatilized. It is given (one-twelfth of a grain) in gout, rheumatism, and neuralgia. It is sometimes employed in dysmenorrhœa, paralysis, hysteria, and disorders dependent upon spinal irritation.

330. Tests:—

1. The general reagents give precipitates with veratrine.
2. "With nitric acid, veratrine forms a yellow solution, and, by contact with sulphuric acid, it first assumes a yellow color, which soon passes to reddish yellow, then to an intense scarlet, and after a while, to violet red. On triturating veratrine with sulphuric acid in a glass mortar, the yellow or yellowish-red solution exhibits, by reflected light, a strong, greenish-yellow fluorescence, which becomes more intense on adding more sulphuric acid. Heated with concentrated hydrochloric acid, it dissolves with a *blood-red color*."—U. S.

Selmi has found in the viscera ptomaines that act like this poison.

331. Aconitine ($C_{33}H_{43}NO_{12}$). It was discovered by Geiger and Hesse in 1832. From *Aconitum Napellus*. It exists in an amorphous and crystalline form, is inodorous, and has a bitter and acrid taste. It is used in the form of an ointment for neuralgia. It is, possibly, the most powerful poison known. The medicinal dose is $\frac{1}{130}$ of a grain. It is doubtful if the alkaloid can be administered internally with safety; one-tenth grain can be regarded as a fatal dose. When taken in poisonous doses, the symptoms come on rapidly. There is diminished sensibility; the skin loses its *sensation*, whilst there is deafness and ringing in the ears, dimness and loss of sight; the pulse is low, feeble, and irregular, becoming at last almost imperceptible, with clammy,

cold sweats; finally, after a few convulsive gasps, the patient expires. In treating, evacuate the contents of the stomach. Brandy and ammonia may be used as stimulants. The following substances are recommended: Vegetable infusions containing tannic acid, iodine in iodide of potassium, also a dilute solution of nux-vomica; strong tea and coffee can be given. The post mortem appearances are characterized by general venous congestion, the brain, liver, and lungs being more or less engorged, and usually accompanied by signs of gastro-intestinal irritation.

It is separated from the plant (roots) or from animal tissues by extracting with alcohol feebly acidulated with tartaric acid, evaporating the extract at a low temperature, 60° C.; redissolve in water, treat with ether to remove impurities, and precipitate with sodium bicarbonate, and recrystallize.

The physiological action of aconitine is excessively energetic—so much so as to render working with it a matter of considerable pain and difficulty. It is soluble in 726 parts of cold water (more soluble in hot water), twenty-four parts of ninety per cent. alcohol, benzene (sparingly when cold), freely soluble in chloroform, soluble in amyl alcohol; does not dissolve in petroleum benzin or carbon disulphide.

332. Tests:—

1. The general reagents give precipitates with aconitine.
2. The physiological action is its chief test. If it is rubbed on the inside of the gums (dilute solution), it produces a sense of tickling and numbness.

NOTE.—The small quantity required to produce death, the symptoms, and the physiological action, are indications of as much importance as the chemical tests for this poison.

333. Atropine ($C_{17}H_{24}NO_3$) was first announced by Brandes in 1819, and in 1833 by Mein, a German pharmacist, who obtained it pure. It is found in the roots, leaves, and berries of the *atropa belladonna* or *deadly nightshade*, in about .5 per cent. The fatal dose is two grains; the medicinal dose for hypodermic injection should not exceed $\frac{1}{250}$ grain. Symptoms: The

patient is drowsy and giddy; the pulse is strong and rapid, the action of the heart being increased; the eyes are prominent and sparkling, and the pupils always dilated. There is often a desire to micturate or walk, and an inability to do either. As it approaches fatal termination there is delirium and sometimes convulsions; these may alternate, and either may end in death. The post mortem appearances are not well marked. Treatment is by emetics; morphine is sometimes administered. Atropine forms colorless crystals, having a bitter and acrid taste and an alkaline reaction. It is soluble in six hundred parts of cold water, thirty-five parts of boiling water, in three parts of chloroform, in sixty parts of ether, very soluble in alcohol, in amyl alcohol, and benzene forty-two parts, scarcely soluble in petroleum benzin or carbon disulphide. Fixed oils dissolve it. It may be separated from the contents of the stomach by acidulating with twenty per cent. of sulphuric acid, digesting for some time at a temperature not exceeding 70° C., and then reducing any solid matter by friction, and filtering with a Bunsen pump. The acid liquid thus obtained is shaken up with amyl alcohol (to remove the impurities), and after the separation of the amyl alcohol, it is agitated with chloroform, which serves to purify it further; the fluid is now made alkaline and shaken up with ether, and the ether is allowed to evaporate spontaneously. The residue contains the atropine, and in some cases, sulphate of ammonia. If treated with absolute alcohol, the alkaloid is dissolved; the sulphate of ammonia is insoluble.

334. Tests:—

1. The general reagents give precipitates with atropine.
2. "With sulphuric acid, atropine gives a colorless solution, which is neither colored by nitric acid (absence of, and difference from, morphine) nor at once by solution of bichromate of potassium (absence of, and difference from, strychnine), though the latter reagent, by prolonged contact, becomes green. The aqueous solution of atropine, or of any of its salts, is not precipitated by test solution of platinic chloride (difference from most other alkaloids)." — U. S.

3. **Vitali's test:** The dry residue is treated with a little fuming nitric acid, then dried on the water bath, and, when cold, touched with a drop of a solution of potassium hydroxide in absolute alcohol, when, in evidence of atropine, or of its isomers, a *violet color* will be produced, slowly changing to a *dark red*. Strychnine gives a red, brucine a greenish color. The violet color is distinctive for atropine among all the important alkaloids, and gives this test with .000001 of a gram of the alkaloid.

4. The physiological test for the presence of atropine is best tried on the eye of a cat. The pupil-dilating alkaloids are chiefly atropine and its isomers, but it must be noticed that other bodies besides the *solanaceous alkaloids* dilate the pupil—cocaine, digitalis and its active principle, and conine.

335. Nicotine ($C_{10}H_{14}N_2$) is found in the common tobacco plant, which contains from four to eight per cent. of it. It was discovered by Posselt and Reimann in 1828. It is a transparent, colorless, oily, liquid (sp. gr. 1.027), boiling at $247^{\circ}C$. It has an exceedingly acrid taste, even when largely diluted. It is volatile, and when in the state of vapor, very irritating to the nostrils; the odor resembles that of tobacco. It is one of the most active poisons known. It is soluble in water, alcohol, ether, chloroform, turpentine, and the fixed oils. It is strongly alkaline in its reactions, and forms crystallizable salts with the acids. It has the remarkable property of resisting decomposition amid the decaying tissues of the body. Both chloroform and ether extract it from aqueous solutions.

The characteristic symptoms of poisoning by it are vertigo, nausea, vomiting, extreme prostration, trembling of the limbs, etc.; respiration is difficult, the skin cold and clammy. The poison is very rapid in its action, and when taken in poisonous doses (one drop usually fatal), death occurs in a few minutes, even equaling hydrocyanic acid in the rapidity of its action. In treating, remove the poison by emetics, etc. Allay pain with opium, or its equivalent, and preserve power with stimulants. The post mortem appearances are not very characteristic. The poison should be looked for in the lungs, liver, and stomach.

Nicotine and conine are separated in the same manner from organic matters. The substances are digested with water, acidulated with H_2SO_4 , at a temperature not exceeding 40°C ., and filtered. To the filtrate concentrated alcohol is added, the liquid refiltered, and from the filtrate the alcohol is separated by distillation. On cooling, the acid liquid is agitated with benzene, and the latter separated. The fluid is now rendered alkaline with ammonia, and shaken up once or twice with its own volume of petroleum ether; the latter is separated and washed with distilled water, and the alkaloid is obtained almost pure. *If the petroleum ether leaves no residue, it is certain that the alkaloid was not present in the part examined.*

The oxalate of nicotine is the best salt from which to regenerate nicotine in a pure state.

336. Tests:—

1. Nicotine is precipitated by alkalies, and by many oxyhydrates—lead, copper, etc. Light changes it to a yellow or brown color, and it becomes thick; in which state it leaves, on evaporation, a brown resinous substance, partly soluble in petroleum ether.

2. It gives, from ethereal solution, needle-like crystals when treated with a solution of iodine in ether. The crystals form in a few hours.

3. Chlorine gas colors nicotine blood red or brown; the product is soluble in alcohol, and on evaporation separates in crystals.

4. A drop of nicotine poured on dry chromic acid blazes up and gives the odor of tobacco. The general reagents give precipitates.

NICOTINE.	CONINE.
Tobacco odor.	"Mousy" odor.
Freely soluble in water.	Sparingly soluble in water.
No crystals with HCl fumes.	Crystals with HCl fumes.
AgNO_3 gives a white precipitate.	AgNO_3 gives a dark-brown precipitate.
Does not coagulate albumin.	Coagulates albumin.
Gives <i>crystalline</i> precipitates with aqueous solution of HgCl_2 .	Similar precipitates with HgCl_2 are <i>amorphous</i> .

337. Conine ($C_8H_{15}N$) is an alkaloid from the poison hemlock. The death of Socrates is generally believed to have been due to this poison. The alkaloid is most abundant in the fruit of the plant, containing about one per cent. It was first obtained as an impure sulphate by Giseke in 1827. One drop may be regarded as a fatal dose. The symptoms are a gradual and complete paralysis of the extremities, enlargement of the pupils, and loss of power. The paralysis gradually extends to the muscles of respiration, and the patient dies of apnœa. The characteristic post mortem appearances are congestion of the stomach and lungs, and more or less congestion of the brain. The blood remains fluid, and there is little evidence of poison in the intestines. In treating, remove the poison by emetics and the stomach pump; then give stimulants.

Nicotine and conine are volatile alkaloids, and are liquids at ordinary temperatures. They are colorless, oily, and volatile. Conine boils at $163^{\circ}C$. One part is soluble in one hundred parts of water, six parts of ether, and in almost all proportions of amyl alcohol, chloroform, and benzene. It ignites easily, and burns with a smoky flame. It acts as a strong base, precipitating the oxides of metals and alkaline earths from their solutions. It coagulates albumin. (It is written coniine, conia, conicine.)

338. Tests:

1. The general reagents give precipitates with conine.
2. A crystal of $K_2Cr_2O_7$ is put at the bottom of a test tube, and some dilute sulphuric acid with a drop of the supposed conine added. On heating, the butyric acid reveals itself by its odor. Butyric acid is formed by heating $K_2Cr_2O_7$ with dilute H_2SO_4 and conine.
3. When dropped into a solution of alloxan, the latter is colored, after a few minutes, an intense purple red, and white needle-shaped crystals are separated, which dissolve in cold potash-lye into a beautiful purple blue, and emit an odor of the base.

339. Caffeine ($C_8H_{10}N_4O_2$) was first discovered by Runge in 1821. Oudry found it (*theine*) in tea in 1827. Mulder Jobest, in 1838, showed that caffeine and theine were identical.

The average percentage is as follows :

In tea (prepared leaf of *Camellia Thea*), two to three per cent.

In coffee (dried seed of *Coffea arabica*), one per cent.

In guarana (crushed seed of *Paulinia sorbilis*), four per cent.

In mate (leaf of *Ilex paraguayensis*), one-half per cent.

In cola nut (seed of *Sterculia acuminata*), two per cent.

Caffeine is a strong base. It is without odor, and has a bitter taste. The medicinal dose is three grains. Caffeine is remarkable for containing a larger proportion of nitrogen than almost any other proximate vegetable principle, in this respect equaling some of the most highly animalized products. It dissolves in 68 parts of cold water, 10 parts of boiling water, in 35 parts of ordinary alcohol, in 476 parts of ether, in 8 parts of chloroform, in 4,000 parts of petroleum benzin. Exhaust the substance with boiling water, evaporate the filtrate with one-half its weight of magnesia and about its weight of ground glass. The residue is pulverized, and treated with eight times its weight of ether for twenty-four hours, filtered, and the residue again treated with ether; the ether is evaporated and the residue weighed. A smaller quantity of chloroform will do; but the product is not so pure an alkaloid. Or this method can be used: Exhaust the bruised coffee by successive portions of boiling water, unite the infusion, add acetate of lead, filter, decompose the lead with H_2S , filter, concentrate by evaporation, neutralize with ammonia; the caffeine is precipitated.

340. Tests:—

1. A portion of the solid in a white porcelain dish is heated on the water bath with a few drops of HCl , a minute fragment of $KClO_3$ is added, the mixture evaporated to dryness, and well dried on the water bath. When cold, the residue is slightly

moistened with ammonia water, applied by the point of a glass rod: a purple color is obtained. It has a reddish-yellow to pinkish color before the action of ammonia. .00005 gram gives this test.

2. It crystallizes in long, slender, flexible, white crystals of silky lustre. It requires a magnifying power of three hundred diameters to bring these out nicely.

3. It is distinguished from most other alkaloids by non-precipitation with potassium mercuric iodide, by yielding cyanide when heated with soda-lime, by dissolving in water, and from acidulous mixture by dissolving in chloroform.

4. Contact with H_2SO_4 should not cause coloration, and on heating at 100°C ., it should darken but slowly. Contact with cold (colorless) nitric acid should not give immediate coloration. When heated in a test tube, it sublimes, leaving no residue.

341. Cocaine ($\text{C}_{17}\text{H}_{21}\text{NO}_4$) was discovered by Lossen in 1865. It is the chief alkaloid of the *Erythroxylon coca* leaf. The hydrochlorate is the chief form of the alkaloid in general use. Cocaine melts at 98°C . It has a bitter taste, and is without odor. It is very slightly soluble in water, soluble in alcohol, ether, chloroform, benzene, petroleum benzin, disulphide of carbon, and in fixed and volatile oils. The cocaine solutions have a strongly alkaline reaction. It is removed from aqueous solution of its salts by adding ammonia to liberate the alkaloid, avoiding an excess, and shaking out with ether, chloroform, benzene, or petroleum benzin. From etherial solutions the alkaloid is taken up by slightly acidulated water, upon agitation.

342. Tests:—

1. It has an intense local anæsthetic and blanching effect upon the mucous membrane. A valuable reagent in minor surgical operations.

2, Mayer's solution, iodine in iodide of potassium, phosphomolybdate, tannin, mercuric chloride (in concentrated solutions), with red color. Caustic alkalies, platinum chloride, gold chloride, alkaline carbonates, cause precipitates. When paper is wet

with a drop of ferricyanide and a drop of ferric chloride, on adding a drop or two of the alkaloid, a reduction takes place, and Prussian blue is formed in this order: morphine, in one-half a minute; cocaine, one and one-half minutes; brucine, six minutes; quinine, seven minutes; cinchonine, ten minutes; strychnine, veratrine, each fifteen minutes (Curtman).

343. The salts of the alkaloids are more soluble in H_2O than the *alkaloids*, and are generally used for the solutions to be tested. After the alkaloids and volatile bodies are removed by the treatment before described in No. 302, the organic matter is removed, in order to dissolve out the metals more completely. From one hundred to five hundred grams of the contents of the stomach or other organ are mixed in a large retort (it should only fill one-third of the retort), with twenty-five per cent. of $KHSO_4$ and a quantity of fuming HNO_3 , equal in weight to the organic matter taken, is added. The reaction is at first violent, but must afterwards be assisted by gentle heat. Any thing that may come over is caught in a receiver and saved. H_2SO_4 is added in large excess, and the mixture heated to near the boiling point of the acid. This may have to be repeated. When the liquid has cooled, add a few crystals of KNO_3 , and again heat until white fumes are given off: a clear liquid, which solidifies on cooling, contains, in the form of sulphate, all the metals as bases. Now dissolve in boiling H_2O , and add what is in the receiver, if any, and dilute the whole to one liter.

The solution, without previous filtration, is then electrolyzed by means of a battery. If Hg is present, or sought, use gold electrode; otherwise platinum will do. From this solution the bases can be separated and identified by the group reagents. If the solution is too acid, it can be removed by evaporation at a gentle heat.

The tests for the inorganic poisons are sufficiently described where they occur in the body of the book.

344. Antimony. The most important compound to the toxicologist is tartar emetic ($KSbOC_4H_4O_6$). Discovered in 1831

by Adrian de Mynsicht. It has small transparent crystals, which become opaque and white on exposure to air. It has a sweet, and, afterwards, metallic taste, and a feebly acid reaction. It is soluble in seventeen parts of cold water and three parts of boiling water; insoluble in alcohol, which precipitates it as a crystalline powder from its aqueous solution.

Ten grains is the smallest dose reported to have proved fatal. The medicinal dose is from one-twelfth to one-sixth of a grain. The poisonous symptoms are metallic taste, nausea, vomiting, frequent hiccough, burning pain in the stomach, colic, frequent stools and tenesmus, small, contracted, and accelerated pulse, coldness of the skin, difficult and irregular respiration, painful cramps in the legs, prostration and death. It was formerly much used as a sedative, antiphlogistic, diaphoretic, and expectorant. It is sometimes used as a counter-irritant, mixed with lard. In some rare cases vomiting and purging do not take place, but the other symptoms are aggravated. The post mortem appearances are general congestion, a fluid condition of the blood, and intense vascularity of the digestive organs. Treatment: If the patient has not vomited, tickle the throat with a feather, or give emetics; tannic acid is given to form an inert tannate of antimony; if the vomiting is excessive, give an injection of laudanum or morphine.

It can be known from most other metallic poisons from the fact that with ferrocyanide of potassium it does not give a precipitate. It is easily identified by Marsh's test, Reinsch's test, or by sulphuretted hydrogen. It is well to dissolve out the poison by hydrochloric and tartaric acids, the latter to dissolve the antimony that may be there that is not combined already with tartaric acid.

For tests see No. 155.

345. Phosphorus was discovered in urine by Brandt in 1669. In 1769, Gahn discovered it in bones. It is always found in combination, never free, its chief source being calcium phosphate. It should be handled with care, and always cut under water. Its specific gravity is 1.83; its melting point is 44° C. It is insoluble in water, soluble in 350 parts of absolute alcohol, in

80 parts of absolute ether, in 50 parts of any fatty oil. Bisulphide of carbon will dissolve eighteen times its weight of phosphorus without losing its fluidity (Vogel). (The red or amorphous phosphorus has a specific gravity of 2.11, and is insoluble in bisulphide of carbon, alcohol, and ether. It is but little acted upon in the air, and is not poisonous.) It is given as a nutritive stimulant to the nervous system, in neuralgia, mania, chronic eczema, and other affections of the skin. The medicinal dose is $\frac{1}{100}$ to $\frac{1}{75}$ of a grain. Poisoning by it has been confined mostly to the use of friction matches and the phosphorus paste used for rat poison. When taken internally, it enters the circulation, imparts to the breath, urine, and sweat, a garlic odor, and makes the secretions luminous in the dark. The vapor of phosphorus causes a necrosis of the jaw bone. Symptoms: Besides those above described, there is a feeling of lassitude, nausea, and great thirst; cold perspiration, and feeble and irregular pulse; the abdomen becomes tender to the touch; the extremities, cold; pulse, imperceptible; and other symptoms of collapse. Death may take place in from one to three days. The smallest fatal dose was in the case of a child that died after sucking two matches, the estimated quantity being about $\frac{1}{50}$ of a grain. Treatment: Sulphate of zinc should be given in three-grain doses every five minutes until vomiting is induced; opium, to restrain the emesis, should be administered in such doses as the stomach will retain. Sulphate of magnesium should be used as a quickly acting purge, and symptoms treated upon general principles. The post mortem appearances are those of a corrosive irritant poison; blood is often found in the bladder, intestines, and pleural cavity. There is fatty change in the liver, kidneys, glands of the stomach, heart, and muscles. For tests see Nos. 107, 215, 216, 217, 218, 303.

When it is tested by distilling it over in the dark, alcohol, ether, and oil of turpentine prevent the occurrence of the luminous appearance until they have distilled over.

1. *Hofmann's test*: Mix the viscera with water, and a little sulphuric acid. Now distill it until two drachms of liquid are

obtained ; to this add a few drops of sulphide of ammonium, and evaporate the liquid to dryness in a porcelain dish. If phosphorus is present in minutest quantity, a drop of a solution of ferric chloride will produce a deep violet and brownish color that is evanescent.

2. *Dusart's test*: Consists in passing pure hydrogen gas, evolved in a separate vessel, through the solution supposed to contain phosphorus, which solution has been previously warmed to about 50° C. The gas then is allowed to issue from a fine jet, and is lighted. If phosphorus is present, the flame shows a *green color* in the center.

346. The mercury compound of most importance is corrosive sublimate (HgCl_2). It is soluble in sixteen parts of cold water, two parts of boiling water, three parts of alcohol, four parts of ether. When heated to 265° C., the salt fuses ; at a higher temperature, it sublimes unchanged and without residue. Ether is capable of removing corrosive sublimate, to a considerable extent, from its aqueous solution when agitated with it. Sulphuric, nitric, and hydrochloric acids dissolve it without alteration.

Corrosive sublimate has the property of retarding putrefaction. Animal matters immersed in its solution shrink, acquire firmness, assume a white color, and become imputrescible. On account of this property it is usefully employed for preserving anatomical preparations.

Corrosive sublimate is a very powerful poison, operating quickly and producing violent effects. It is less apt to salivate than most other mercurials. In minute doses, it produces a slight increase in the frequency of the pulse, and in the secretions from the skin and kidneys. It may purge, but this effect can be modified by combining it with a little opium. It is used in nearly all stages of syphilis, in chronic cutaneous affections, and in obstinate chronic rheumatism ; externally it is used as a stimulant and escharotic. The medicinal dose is from one-twelfth to one-eighth grain. In poisonous doses, it produces heat

in the throat, pain in the stomach and bowels, thirst, vomiting of bloody mucous, diarrhœa, bloody stools, small rapid pulse, difficult respiration, fainting, convulsions, and death. Death may take place in half an hour, or it may be delayed for weeks. Treatment: White of egg in milk; albumin in some form, followed by emetics, with Peruvian bark, meconic acid, lime water, ferrocyanide of potassium. It is of the utmost importance *in all poisons* that whatever antidote is given it should be used without delay, and in this respect the one nearest at hand may be considered the best. The pathological effects are too various to be distinctive. In acute poisoning the changes are great and striking. After a violent death from corrosive sublimate, the escharotic whitening of the mouth, throat, and gullet will be seen. The mucous membrane from mouth to anus is more or less affected and destroyed, the stomach congested, may be destroyed; sometimes the coats are black.

The main channel by which the absorbed mercury passes out of the body is by the kidneys. If an insoluble compound is formed, it passes off by the bowels.

For the tests see No. 139.

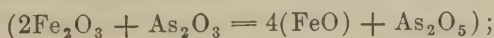
Reinsch's test gives a stain that resembles As.

A piece of polished gold immersed in a clear solution of corrosive sublimate and touched with the point of a pen knife (to make a battery) forms a white stain.

347. Arsenic is found combined with many of the metals; as, Ag, Cu, Fe, etc. Its *principal source* is the arsenical pyrites. The substance used in the arts under the name of arsenic is really the oxide of arsenic (arsenious anhydride As_2O_3). It is entirely volatilized by heat at 204°C . The specific gravity is 3.7. It has little, if any, taste. It is soluble in from thirty to eighty parts of water, the solubility varying with its physical condition; it is slowly but completely soluble in fifteen parts of boiling water, sparingly soluble in alcohol. It is freely soluble in HCl , the alkalies, and their carbonates, and moderately soluble in glycerin. The transparent form is more soluble than the opaque.

When taken in large doses, all the compounds of arsenic are violent irritants or escharotics. Medicinal doses are alteratives affecting the nutrition of the nervous system, and are given in nervous debility, chorea, and chronic malaria. It is the chief ingredient in nearly all the empirical remedies for the cure of cancer by external application. It has a wide application in skin diseases. It is used in many paints, bug and rat poisons, pyrotechny, medicines, and in making aniline dyes. It is no longer considered a cumulative poison; that is, the continued use of frequent small doses is not believed to possess the power of gradually and silently accumulating in the body, and then suddenly breaking out with dangerous or fatal violence. The poisonous symptoms are bad taste, fetid state of the mouth, often ptyalism, continued hawking, a feeling of contraction in the œsophagus and pharynx, hiccough, nausea, burning pain at præcordia; inflammation of the mouth, throat, and œsophagus; irritable stomach, vomiting; black, fetid stools; small, frequent, irregular pulse; great thirst, difficult respiration, cold sweats, suppression of urine (it may be scanty, or bloody, or contain albumin); the mind is generally clear. The symptoms may terminate in many ways: (1) Convulsions, in fits of an epileptic nature; (2) collapse, with or without pain, and vomiting or diarrhœa; (3) intense coma; (4) immediate death, as if by shock; (5) it may act like cholera, and deceive the practitioner. Treatment: Give emetics of sulphate of zinc or sulphate of copper; afterwards give milk and white of eggs. The chemical antidote, due to Bunsen and Berthold, is the hydrated sesquioxide of iron.

The chemistry of the operation is thought to be as follows: The arsenious acid is oxidized to arsenic acid by the oxygen of the iron, while the iron is reduced to the protoxide



now this protoxide of iron combines with acid to form an insoluble or difficultly soluble arsenate of iron, about fourteen parts of the moist, *recently precipitated* iron being used to one of arsenic. The hydrated sesquioxide is made by precipitating a ferric salt of iron by an excess of ammonia, filtering through muslin, pocket

handkerchief, or anything handy, and washing out the ammonia. If the arsenic is not in solution, the hydrated oxide of iron or magnesia is of no use.

Arsenic has the power of preserving the body from decay. The blood is usually fluid, but this is the case with most animals that die a violent death; the organs have the appearance usually produced by irritant poisons.

For tests see No. 153.

Christison, on poisons, regards the confirmation by the following reagents as *unimpeachable evidence of the presence of arsenic*. While there are fallacies in any one test taken alone, there is "no other substance in nature (but arsenic) which produces the same effects as it with the whole three tests in succession." These are: (1) With H_2S . (2) Hume's test—ammonia nitrate of silver. It should be made fresh each time it is required. Add to a solution of nitrate of silver a weak solution of ammonia, drop by drop, until the brown precipitate first produced is *nearly* dissolved, and pour off the clear solution; this gives, with a solution of arsenious acid, a bright yellow precipitate of arsenite of silver. Some trouble is often experienced in getting this precipitate, as the reagent is decomposed by organic matter. (3) Scheele's test—the *ammonia sulphate of copper*. It is made by adding to a weak solution of copper, ammonia, drop by drop, until the precipitate first formed is nearly dissolved; the clear liquid is now decanted and used. It gives, with arsenious acid, a light apple-green precipitate of arsenite of copper (Scheele's green). It can be also determined by Bloxam's, Marsh's, Reinsch's, and Fleitman's tests, or those given under No. 153.

348. Lead. The effects of lead in its various combinations are those of a sedative and astringent. It is used internally for reducing the action of the heart and arteries, and for restraining inordinate discharges; externally, as an abater of inflammation. When taken in small quantities often repeated, it acts injuriously on the nervous system, producing pain with sinking about the navel, the seat of the colon; constipation, loss of appetite, thirst,

fetid odor of the breath, and general emaciation, especially of the muscles of the arms, and a blueness of the edges of the gums. The effect on the nervous system is numbness of feeling in the skin, trembling of the arms and legs, paralysis of the extensor muscles so that the hand drops; the body becomes emaciated, the legs oedematous, and the person dies exhausted. In acute poisoning these symptoms come on rapidly, and with greater intensity. There is, invariably, constipation from paralysis of the intestinal muscular coat; the urine is scanty and red; violent cramps, cold sweats, paralysis of the lower extremities, and often convulsions and tetanic spasms come on; the mind is usually clear to the last. The *time* death takes place and the *dose* to produce it are quite variable. Treatment: Cause vomiting by sulphate of zinc, warm water, or the stomach pump. Give any soluble alkaline or earthy sulphate. Sulphate of magnesia is one of the best; it can be given in milk mixed with white of eggs. In chronic cases, iodide of potassium is given three times a day in from five to ten grain doses; also, sweetened dilute sulphuric acid. But first and last, great cleanliness is of more importance to the workman than all the doctor's medicine, and at the first indication of lead poisoning, the work must be discontinued, and proper treatment *at once* adopted.

Many of the hair washes or hair restorers are solutions of lead acetate mixed with sulphur.

The acetate and carbonate are the most important salts to the toxicologist. All the soluble salts of lead are poisonous.

For tests see No. 137.

349. Zinc. The acetate of zinc is used almost exclusively as a local remedy, as an astringent collyrium in ophthalmia, and as injections in gonorrhœa after the acute stage has passed. The chloride is used mostly as an escharotic; internally, as an alterative and antispasmodic. The oxide of zinc is used as a cosmetic, tonic, antispasmodic, and astringent. The sulphate is soluble in less than one part of water. This salt is used as a tonic, astringent, and in large doses as an emetic. It is used in dyspepsia, in night sweats of consumption, with extract of belladonna or of

hyoscyamus; sometimes in cholera. The acetate and sulphate are, as a general rule, used in the same class of diseases. The sulphate, in over doses, acts as an irritant poison. It rapidly coagulates albumin and the delicate tissues of the body. The pulse and breathing are accelerated, the voluntary muscles are paralyzed, pupils dilated, coma supervenes, and death comes without a struggle. Treatment: Carbonate of soda with milk, white of egg, tea, etc. Opium is given to relieve pain. The post mortem appearances are inflammation of the intestinal tract; the brain and lungs are generally congested.

In toxicology, the chloride, the acetate, and the sulphate are the most important.

Sulphate of zinc has been very frequently taken by accident or design, but death from it is rare. The infrequency of fatal result is due, not to any inactivity of the salt, but rather to its being almost always expelled by vomiting; so much so that it is often relied upon in poisoning from other substances. It is found in the stomach, liver, and intestines; in some cases in the spleen.

The tests are sufficiently described in No. 175.

350. Copper. The common salts are acetate and sulphate. The local and general action of verdigris (acetate) upon the animal economy and the treatment of its poisoning are the same as those of the sulphate of copper. It is never used internally in *modern* practice. The sulphate is soluble in 2.6 parts of cold water, in one-half part of boiling water; insoluble in alcohol. At a temperature of 230° C., it becomes anhydrous; at a high temperature, it loses its acid and becomes cupric oxide. The sulphate is an irritant or mildly escharotic; when in dilute solution, stimulant and astringent. It is not used internally, except for its influence upon the gastro-intestinal mucous membrane. In chronic diarrhœa with ulceration, it is often a useful remedy. In five grain doses, it is used as an emetic in narcotic poisoning and to dislodge false membrane or foreign bodies from the larynx and œsophagus. Externally it is used in solution as a stimulant to ulcers; as an escharotic for warts, fungus granulations, and

callous edges; and as a styptic to bleeding surfaces. The medicinal dose is one-fourth of a grain, gradually increased; as an emetic, five grains every fifteen minutes. When taken in poisonous doses, it produces a coppery taste in the mouth, nausea, and vomiting; violent pain in the stomach and bowels; frequent black and bloody stools; small, irregular, and frequent pulse; fainting, burning thirst, scanty urine, pain in voiding it, violent headache, cramps, convulsions, and finally death. The best antidote is ferrocyanide of potassium; soap and alkalies are also given; milk and white of eggs. Vessels of copper which are not coated with tin should not be used in pharmacy nor in the household. The post mortem appearances are fatty liver, swollen kidneys, and the mucous membrane of the stomach excoriated. The post mortem appearances are usually confined to the alimentary canal.

The tests are sufficiently described in No. 149.

Of the acids, oxalic and hydrocyanic are the most important. The tests are described in Nos. 222 and 242.

351. We trace the poisons to the circulation, and observe that death is the result; but there is at present no satisfactory theory to account for the fatal effects, or explain how they operated. The blood seems to be so changed by the poison as to render it unfitted to perform its proper functions, but the *modus operandi* is as yet a perfect mystery. Neither the chemist, microscopist, nor physiologist has been able to throw any light upon the changes produced by the poison in the blood or in the organs necessary to life. It has been clearly shown that no substance acts as a poison until it has been absorbed and passed through the arterial capillary system. The sooner the poison reaches the blood the more rapidly does it act, and it depends not so much upon the quantity as the amount absorbed in a given time. The time for this absorption, under favorable circumstances, is only a few seconds. The fatal effects are produced when the absorption takes place more rapidly than the elimination. The fatal proportion of poison present in the blood at any one time is infinitesimally small (one-sixteenth grain of strychnine has caused the

death of a child in four hours). The blood is about one-thirteenth of the body by weight, and the proportion of the poison by weight, compared with the blood, would be only one part in millions. The poison of a cobra is yet in a smaller proportion; but this is not all. The blood, urine, saliva, or milk of an animal poisoned by the cobra, when injected into another animal, will produce death.

As to the *intent*, poisons are divided into criminal, accidental, and suicidal.

The general arrangement of nearly all toxicologists has been based upon the *physiological effects* of poisons. Some authors, however, adopt the more simple plan of arranging them according to their *origin* or natural source, viz.: (1) Mineral, (2) vegetable, (3) animal, (4) gaseous.

CHAPTER VIII.

GENERAL STOICHIOMETRY.

USEFUL CONSTANTS.

I.

1	micromillimeter	=	$\frac{1}{25000}$	of an inch (microscopic unit).
1	gram	=	15.4	grains.
1	kilogram	=	2.2	pounds.
29.57	cubic centimeters	=	1	fluid ounce.
1	liter	=	61	cubic inches or 2.1 pints.
1	meter	=	39.37	inches or 100 centimeters.
1	inch	=	2.5	centimeters or 25 millimeters.
29.92	inches	=	760	millimeters.
33.81	fluid ounces	=	1	liter.
31.1	grams	=	1	Troy ounce.
28.349	grams	=	1	Avoirdupois ounce.
480	grains	=	1	Troy ounce.
437.5	grains	=	1	Avoirdupois ounce.
455.7	grains	=	1	fluid ounce.
46.73	C. c. of hydrogen.	=	1	grain.
100	cubic inches of air	=	31	grains in weight.

Water at 0° C. is 11,160 times heavier than hydrogen. The "crith" is the weight of one liter of hydrogen at 0° C., and 760 millimeters pressure = .0896 grams. The mechanical equivalent of heat is 772 foot pounds for 1° F., or 1,390 foot pounds for 1° C., or 423.6 kilogram meters. The U. S. gallon is to the Imperial gallon as 61,440:76,800, or as 1 is to 1.2.

II. Conversion of thermometric scales (C., Centigrade; F., Fahrenheit; R., Reaumur).

F	C	R
212	100	80
180	100	80
32	0	0

A glance at these figures will show that 180° F. = 100° C. = 80° R., or dividing by 20, 9° F. = 5° C. = 4° R.

To convert—

C.° to F.°, multiply by 9, divide by 5, and add 32.

C.° to R.°, multiply by 4 and divide by 5.

F.° to C.°, subtract 32, multiply by 5, and divide by 9.

F.° to R.°, subtract 32, multiply by 4, and divide by 9.

R.° to C.°, multiply by 5 and divide by 4.

R.° to F.°, multiply by 9, divide by 4, and add 32.

1. Express 40° F. in degrees C.:

$$40 - 32 = 8; 8 \times 5 \div 9 = \frac{40}{9} = 4.4^\circ \text{C.}$$

2. Express — 10° F. in degrees C.:

$$-10 - 32 = -42; -42 \times 5 \div 9 = -23.3^\circ \text{C.}$$

3. At what point, below zero, are the numbers on the scales of Fahrenheit and Celsius identical?

Let x = the number; $32^\circ + \frac{9}{5}$ of $x^\circ \text{C.} = x^\circ \text{F.}$

$$160^\circ + 9x = 5x. \quad -4x = 160^\circ. \quad x = -40^\circ.$$

(The Nos. will agree with *unlike signs* between 11° and 12°).

III. Gases expand $\frac{1}{273}$ part of their volume at 0° C. for every increase in temperature beyond 1° C.; the contraction follows the same law. Expressed decimally, $\frac{1}{273} = .003663$, and is called the coefficient of expansion of gases. The volume of a gas varies *directly* as its absolute temperature, and *inversely* as the pressure to which it is subjected.

RULE—As 273 *plus* given temperature is to 273 *plus* required temperature, so is given volume to required volume.

1. Five hundred C. c. of a gas at 5° C. are heated until they become 700 C. c. Through what number of degrees C. has the gas been heated?

$$500 : 700 :: 273 + 5 : 273 + x.$$

$$500 (273 + x) = 700 \times 278.$$

$$500x = 700 \times 278 - 273 \times 500.$$

$$x = 116.2^\circ \text{C.} - 5^\circ \text{C.} = 111.2^\circ \text{C.}$$

2. Fifty C. c. of air is measured at 12° C. and 750 m. m.
Required, volume of the air at 20° C. and 800 m. m.

$$\begin{array}{l} 800:750 \\ 273 + 12:273 + 20 \end{array} \left. \vphantom{\begin{array}{l} 800:750 \\ 273 + 12:273 + 20 \end{array}} \right\} :: 50:x.$$

$$x = \frac{50 \times 750 \times 293}{800 \times 285} = 48.19 \text{ C. c.}$$

3. A liter of air is measured at 0° C. and 700 m. m. What volume will it occupy at 720 m. m. and 18° C.?

$$\begin{array}{l} 273:273 + 18 \\ 720:700 \end{array} \left. \vphantom{\begin{array}{l} 273:273 + 18 \\ 720:700 \end{array}} \right\} \begin{array}{l} \therefore 1,000:x. \\ \therefore 1,000:x. \end{array} \text{ Solve for } x.$$

IV. The specific gravity of a body is its weight compared with the weight of an equal volume of the standard. Hydrogen and air are the standards for gases, water for liquids and solids. In the above, normal conditions of temperature and pressure are understood.

W equals weight in air; w equals loss of weight in water.

$$\therefore \text{Specific gravity equals } \frac{W}{w} \text{ (for solids).}$$

1. A body weighs in air, 450 grams; in water, 240 grams.
Required, the specific gravity.

$$450 - 240 = 210; 450 \div 210 = 2.2, \text{ nearly.}$$

2. Five grams of a powdered mineral is put into a counterpoised sp. gr. bottle which holds 100 grams of water; the bottle is then filled with water. Thus charged, it is found to weigh 102.6 grams. What is the specific gravity of the mineral?

$$102.6 - 5 = 97.6; 100 - 97.6 = 2.4, \text{ therefore } 5 \div 2.4 = 2.08.$$

3. What is the volume of 20 grams of HCl? The specific gravity of the gas is 18.25, and .0896 gram of H occupies 1 liter.
 $.0896 \times 18.25 = 1.635$ grams of HCl occupy 1 liter; one gram of HCl occupies $\frac{1}{1.635} = .6116$ of a liter, and 20 grams occupy $.6116 \times 20 = 12.232$ liters.

(a) The density of a simple gas is its atomic weight; if this is divided by 14.43 it will give the density as compared with air.

Oxygen is 16 times heavier than hydrogen, or $\frac{16}{14.43} = 1.1$ times heavier than air.

(b) The density of a compound gas is $\frac{1}{2}$ its molecular weight. The molecular weight of $\text{CO}_2 = \frac{12 + 32}{2} = 22$; *i. e.*, 22 times heavier than hydrogen, or $\frac{22}{14.43} = 1.5$ times heavier than air.

4. A piece of cork weighs in air 82 grams. A tin sinker weighs in water 785 grams. The two together weigh in water 355 grams. What is the specific gravity of the cork?

Let a = wt. of cork in air.

Let b = wt. of sinker in water.

Let c = wt. of both in water.

$$\text{Then sp. gr. of cork} = \frac{a}{a + b - c} = \frac{82}{82 + 785 - 355} = .16.$$

V. To calculate the percentage composition of a compound from its formula:

1. Calculate the percentage composition of potassium nitrate (KNO_3): $\text{K} = 39$, $\text{N} = 14$, $\text{O}_3 = 48$; $\text{O} = \frac{48 \times 100}{101}$; $\text{N} = \frac{14 \times 100}{101}$; $\text{K} = \frac{39 \times 100}{101}$. The molecular weight is $(39 + 14 + 48) = 101$.

2. How many pounds of mercury and chlorine in 112 pounds of pure corrosive sublimate (HgCl_2)? $\text{Hg} = 200$, $\text{Cl}_2 = 71$; 200 parts of Hg combine with 71 parts of chlorine. $\text{Hg} = \frac{200}{271}$ of 112; $\text{Cl} = \frac{71}{271}$ of 112.

3. How much mercury is contained in 125 pounds of an ore of which 75% is mercuric sulphide (HgS)? $\text{Hg} = 200$, $\text{S} = 32$; 75% of 125 pounds = 93.75 pounds of HgS .

$$\text{Hg} = \frac{200}{232} \text{ of } 93.75; \text{S} = \frac{32}{232} \text{ of } 93.75.$$

VI. To calculate the quantity of material to yield, liberate, or produce a given weight of a substance.

1. We want 50 pounds of oxygen. How many pounds of potassium chlorate must we take? $\text{KClO}_3 = \text{KCl} + \overline{\text{O}_3}$. The molecular weight of KClO_3 is ($\text{K} = 39$, $\text{Cl} = 35.5$, $\overline{\text{O}_3} = 48$) 122.5; $\text{O} = \frac{48}{122.5}$; $48:122.5::50:x$; whence $x = 127.6$ pounds.

From IV. the *volume* can be easily calculated.

2. Silver is to be precipitated from 100 grams of silver nitrate by means of metallic zinc. How much Zn will be required? $2\text{AgNO}_3 + \text{Zn} = \text{Zn}(\text{NO}_3)_2 + \underline{\text{Ag}_2}$. The molecular weight of $\text{AgNO}_3 = 170$. \therefore 340 parts of AgNO_3 require 65.2 parts of zinc.

One gram of AgNO_3 requires $\frac{65.2}{340}$ grams of zinc.

One hundred grams of AgNO_3 require $\frac{65.2}{340} \times 100 = 19.17$ grams of zinc.

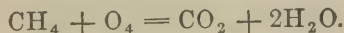
3. What quantities of mercury and of sulphuric acid are necessary to furnish a kilogram of sulphurous anhydride?



$200 + 196 = 296 + 36 + 64$. Dividing by 64, we have 3.12 and 3.06, the respective amounts.

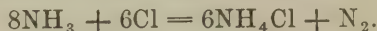
VII. Combinations and decompositions of bodies in the gaseous form.

1. How many cubic feet of oxygen are required to consume completely one cubic foot of marsh gas, and how many cubic feet of carbonic anhydride and of water will be formed?



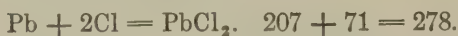
Volumes $2 + 4 = 2 + 4$ (H_2O itself is two volumes). \therefore Two cubic feet of marsh gas require four cubic feet of oxygen, and there are formed two cubic feet of carbonic anhydride and four cubic feet of water vapor; now, one cubic foot of marsh gas requires two cubic feet of oxygen, and one cubic foot of carbonic anhydride and two cubic feet of water vapor are formed.

2. x volumes of ammonia are decomposed by chlorine. How many volumes of chlorine are required?



Sixteen volumes of NH_3 require 6 volumes of Cl ; 1 volume of NH_3 requires $\frac{3}{8}$ volume of Cl ; x volumes of NH_3 require $\frac{3}{8}x$ volumes of Cl .

3. How many liters of chlorine must be used to form 100 grams of lead chloride (PbCl_2)?



From the equation we see that a molecular weight of lead chloride requires a molecular volume of chlorine to form it.

11.2 liters of chlorine gas weigh 35.5 grams; so it requires
22.4 liters of chlorine $\therefore 1 \text{ gram} = \frac{22.4}{278}$,

$$100 \text{ grams} = \frac{22.4}{278} \times 100 = 8.06 \text{ liters, nearly.}$$

4. If air contains 23% by volume of oxygen, how many liters of air will be necessary to burn completely 1 kilogram of carbon? $\text{C} + \text{O}_2 = \text{CO}_2$; 12 parts, by weight, of carbon combine with 32 parts of oxygen, or 1 kilogram of carbon requires $2\frac{2}{3}$ kilograms of oxygen. 11.2 liters of hydrogen weigh 1 gram; air, being 14.43 times heavier, weighs 14.43 grams, or 1 liter weighs $\frac{14.43}{11.2} = 1.29$ grams. A kilogram of air occupies as many liters as 1.29 is contained in 1,000, or 775.2 liters. $2\frac{2}{3}$ kilograms will have a volume of $775.2 \times 2.66 = 2,062$ liters, if the air was pure oxygen; but as it contains only 23% of oxygen, it will be as many times 2,062 as 23 is contained in 100 = 4.35 times; $2,062 \times 4.35 = 8,969.7$ liters of air.

VIII. How the atomic weight of an element is obtained.

1. If it is a gas, by comparing the weights of the same volume under like conditions of temperature and pressure with hydrogen.

2. If a metal, the product of its specific heat by its atomic weight is a constant quantity, about 6.34. The specific heat of a body is the amount of heat required to raise a unit weight of the substance from 0° C. to 1° C., the thermal unit being the amount of heat required to raise one gram of water through 1° C.

In a general way, by making an analysis of their compounds—if possible, gaseous compounds—and carefully comparing the results.

Sometimes a formula is assumed. The formulæ of compounds used are very necessary. Much assistance is derived from (1) Mitscherlich's law of isomorphism, (2) law of specific heat, (3) by substituting in equal successive portions, as from H_2O , KHO , K_2O , etc.

The density of a gas is one-half its molecular weight.

1. Stas found, after adding 7.25682 grams of potassium chloride to 10.51995 grams of silver dissolved in nitric acid, that .0194 grams of silver remained in solution. Calculate from these data the atomic weight of potassium (the other atomic weights supposed to be known). $10.51995 - .0194 = 10.50055$, the amount of silver used.

At. wt. Ag : at. wt. Cl :: wt. Ag : wt. Cl.

108 : 35.5 :: 10.50055 : x , or 3.45157.

$7.25682 - 3.45157 = \text{wt. of K, or } 3.80525$.

Wt. Cl : wt. K :: at. wt. of Cl : at. wt. K.

$3.45157 : 3.80525 :: 35.5 : x, x = 39.1$.

2. Erdmann and Marchand obtained 109.6308 grams of mercury from 118.3938 grams of the red oxide. Calculate the atomic weight of mercury, supposing that of oxygen to be known.

$\text{HgO} - \text{Hg} = \text{O}$.

$118.3938 - 109.6308 = 8.7630$, the weight of the oxygen.

Wt. of O : at. wt. of O :: wt. Hg : at. wt. of Hg.

$8.7630 : 16 :: 109.3608 : x, x = 200$, nearly.

3. Stas found that 91.462 grams of metallic silver, when heated in a stream of chlorine, yielded 121.4993 grams of pure

silver chloride. Calculate from this the atomic weight of chlorine. $121.4993 - 91.462 = 30.0373$ the amount of Cl.

Wt. of Ag : at. wt. Ag :: wt. Cl : at. wt. Cl.

91.462 : 108 :: 30.0373 : x , solve for x .

IX. The percentage composition of a compound being given. Required, its empirical formula.

1. A substance has been found to contain in 100 parts :

Hydrogen.....	2.04 \div 1 = 2	} H_2SO_4 .
Sulphur.....	32.65 \div 32 = 1	
Oxygen.....	65.31 \div 16 = 4	
	<hr/> 100.00	

RULE—Divide the percentage by the atomic weight, reduce the quotients to their simplest relation in whole numbers.

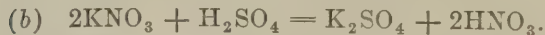
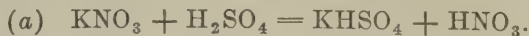
2. Potassium equals..... 28.73 \div 39 = .73 = 1 }
 Hydrogen "73 \div 1 = .73 = 1 } KHSO_4 .
 Sulphur " 23.52 \div 32 = .73 = 1 }
 Oxygen " 47.02 \div 16 = 2.93 = 4 }

100.00
3. Iron equals..... 70.01 \div 56 = 1.25 \div 62 = 2 }
 Oxygen equals..... 29.99 \div 16 = 1.87 \div 62 = 3 } Fe_2O_3 .

100.00

X. Students have experienced some difficulty in solving problems when the bye products are of two different kinds and vary in amount.

1. How much (molecular weight) KHSO_4 , K_2SO_4 , and HNO_3 will be formed when 120 parts of KNO_3 and 94 parts of H_2SO_4 are used in making nitric acid.



(d) There will be as many parts of nitric acid formed as there are of potassium nitrate taken.

(e) If equal quantities are taken, only the bisulphate (KHSO_4) is formed.

(f) If two parts of KNO_3 to one of H_2SO_4 , only the normal sulphate (K_2SO_4) is formed.

(g) The bisulphate (KHSO_4) is *first* formed.

(h) The number of parts of normal sulphate (K_2SO_4) is found by subtracting the number of parts of sulphuric acid from the number of parts of potassium nitrate.

(i) If the number of parts of normal sulphate be subtracted from the number of parts of sulphuric acid, it leaves the number of bisulphate.

The answer can now be written out, as follows:



XI. Thermal units.

The *specific heat* of a body is expressed by a number which shows the amount of heat necessary to raise a given weight of the body one degree (0° to 1° C.) of temperature as compared with the amount necessary to raise the same weight of water one degree.

The *latent heat* of a liquid body means the amount of heat required to change the body from the solid to the liquid state without change of temperature. The latent heat of a vapor is the amount of heat necessary to change the body from the liquid to the vapor form without changing its temperature.

Atomic heat of a body is the amount of heat necessary to raise an atomic weight of the body through one degree of temperature. So far as elementary bodies are concerned, their atomic heats are *inversely* as their atomic weights. The amount of heat required to raise one pound of oxygen 1° C., is one-sixteenth of that required to raise one pound of hydrogen 1° C.

1. Five kilograms of water have to be raised through 10° C. How much charcoal (calling it pure carbon) would it be necessary to burn to do this? Carbon in burning develops 8,080 units of heat (see No. XI.) $8,080:50::1:x$, $x = .00618$ kilograms or 6.18 grams.

2. Eleven hundred and twenty pounds of iron ore have to be raised to the top of a shaft 1,000 feet deep. What weight of charcoal would develop, during its combustion, force enough to do this? $1,120 \times 1,000 = 1,120,000$ foot pounds required. One pound of coal, in its combustion, develops 8,080 units of heat; but the mechanical work which this heat is capable of doing is: $8,080 \times 1,390$, or 11,231,200 foot pounds.

$\therefore 11,231,200 : 1,120,000 :: 1 : x$, when $x = .09$ pound.

3. A piece of zinc falls from a height of 1,000 feet; to what temperature, centigrade, will the zinc be raised by the arrest of motion? When water falls from a height, every 1,390 feet fallen generates 1°C . $1,390 : 1,000 :: 1 : x$, $x = \text{temperature}$, to which water would be raised by a fall of 1,000 feet; $x = .769^\circ \text{C}$.

Sp. heat Zn : sp. heat of $\text{H}_2\text{O} :: \text{temp. of } \text{H}_2\text{O} : \text{temp. Zn}$.

.0927 : 1 :: .769 : x , $x = 8.3^\circ \text{C}$., nearly.

4. How many pounds of carbon must be burned in order to melt just 1,000 pounds of ice? How many to evaporate 100 pounds of water, the temperature of which is 10°C .

The latent heat of water, 79.25, to melt 1,000 lbs. of ice = $1,000 \times 79.25 = 79,250$. The units of heat developed by the combustion of one pound of carbon =

$8,080 \therefore 8,080 : 79,250 :: 1 : x$, $x = 9.8$ pounds of carbon.

For the second part of the question. Units of heat required to raise the water to the boiling point, $100 \times (100 - 10)$, or 9,000. Units of heat required to evaporate the *boiling* water = $535.9 \times 100 = 53,590$. The total units of heat required, $9,000 + 53,590$, or 62,590.

$8,080 : 62,590 :: 1 : x$, $x = \text{carbon required in pounds} = 7.75$.

352. Heating power of coal.

Calorific power of hydrogen.....	34,462
“ “ “ carbon	8,080
“ “ “ sulphur	2,221
Specific heat of carbonic anhydride.....	.2164
“ “ “ nitrogen2440
“ “ “ water vapor.....	.4805
“ “ “ sulphurous anhydride1554

Latent heat of steam (thermal units), 537°C .

Parts of nitrogen to one of oxygen in air (by weight), 3.314.

Weight of 100 cubic inches of air (about 2 grams), 31 grains.

The value of a fuel may be estimated in two ways, as *calorific power* and as *calorific intensity*. Calorific power means the total quantity of heat developed in the combustion of a given weight of the substance; caloric intensity means the maximum temperature developed in the process. The absolute amount of heat *must be constant under all conditions*. The result must be very different in the matter of temperature, as it is influenced by the nature of the products of combustion, the rapidity of the development of heat compared with the rapidity of its dissipation among surrounding bodies.

A fuel may have a *high absolute heating power* and give a low temperature, or a low heating power and give a high thermometric intensity. There are cases in which both of these results are valuable. There being no absolute unit of heat, the heat required to raise one pound of water one degree in temperature (or one kilogram one degree) is usually assumed as the standard.

353. The ultimate analysis (made in the Laboratory of the Experiment Station) of a Colorado coal is as follows:

Carbon	80.00
Nitrogen	1.50
Sulphur	2.00
Hydrogen	6.00
Oxygen	6.20
Ash	4.30
	<hr/> 100.00

From the calorific power of hydrogen we learn that in the combustion of one pound of hydrogen enough heat is produced to raise 34,462 pounds of water one degree in temperature, carbon 8,080, etc.

The calorific power of carbon (8,080) multiplied by the amount $80 = 646,400$ units. From the hydrogen must be subtracted enough to combine with 6.2 pounds of oxygen to form water (in water there is $\text{H} = \frac{2}{18} \text{O} = \frac{16}{18}$, 8 times as much oxygen

as hydrogen); $6.2 \div 8 = .77$ pounds of hydrogen to combine with the 6.2 pounds of oxygen, leaving $6 - .77 = .523$ pounds of hydrogen which can take part in the combustion; this multiplied by the calorific power of hydrogen, $34,462 \times 5.23 = 180,236.26$ units as the value of the hydrogen. The calorific power of sulphur, $2,221 \times 2$ pounds = the heat units for sulphur = 4,442 units. The sum total = $646,400 + 180,236.26 + 4,442 = 831,078.26$ heat units. But heat is required to convert the water formed in the process of combustion (and hygroscopic) into steam, reckoning from 100° C. The amount of water formed will be nine times the amount of hydrogen, $6 \times 9 \times 537 = 28,998$ units, and leaves $831,078.26 - 28,998 = 802,080.26$ heat units for 100 pounds, or 8,020.8 for one pound of fuel. The calorific power of this coal would generate heat sufficient to raise 8,020 pounds of water in temperature 1° C., or $8,020 \div \frac{5}{9} = 14,436$ pounds 1° F.

354. To ascertain the maximum intensity or thermometric value, it is necessary to consider the specific heats of substances resulting from the combustion. This result is obtained by dividing the calorific power by the sum of the products of each of the results of the combustion by its specific heat. In the case of our coal, we have from the combustion of 100 pounds—

$C + O_2 = CO_2$, or 3.66 times the $C = CO_2$;

$$80 \times 3.66 = 292.8 \text{ pounds } CO_2;$$

$H_2 + O = H_2O$, or 9 times the $H = H_2O$;

$$6 \times 9 = 54 \text{ pounds } H_2O;$$

$S + O_2 = SO_2$, or 2 times the $S = SO_2$;

$$2 \times 2 = 4 \text{ pounds } SO_2;$$

making $292.8 + 54 + 4 = 350.8$ pounds of the several products. By the reaction nothing but oxygen has been added. If from this sum (350.8 pounds) the C, H, and S be subtracted, it leaves the amount of oxygen required for their formation ($80 + 6 + 2 = 88$), $350.8 - 88 = 262.8$ pounds of oxygen, deducting the 6.2 pounds found in the coal ($262.8 - 6.2 = 254.6$); this 254.6 pounds of oxygen must come from the atmosphere; to obtain this quantity

of oxygen from the air, it is accompanied by 843.74 pounds of nitrogen (254.6×3.314); the coal contains 1.5 pounds of nitrogen, making a sum total of $843.74 + 1.5 = 845.24$. The specific heat of the *ash* is quite small—about .2, and is usually neglected, not materially affecting the results:

292.8	pounds	CO ₂	×	specific heat	.2164	=	63.36
54	"	H ₂ O	×	"	"	.4805	= 25.94
4	"	SO ₂	×	"	"	.1554	= .62
845.24	"	N	×	"	"	.2440	= 206.23

For 100 pounds of coal = 296.15 for one pound = 2.9615.

It takes as much heat to raise the temperature of the products of combustion from one pound of this coal 1° C. as will heat to the same temperature 2.9615 pounds of water. By dividing the *calorific power* 8,020.8 by this number ($8,020.8 \div 2.96$), we obtain 2,712° C. as the temperature produced by the complete combustion of this coal.

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